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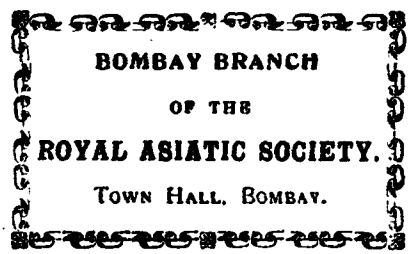

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Errata.

Page 17 line 26 from top *et seq.*, *for* Nillson *read* Nilson.
„ 34 „ 26 „ foot, *for* Nillson *read* Nilson.
„ 141 „ 14 „ top, *for* Picini *read* Piccini.
„ 414 „ 13 „ foot, *for* Giles' *read* Gelis.

PRINCIPLES OF CHEMISTRY

CHAPTER XV

THE GROUPING OF THE ELEMENTS AND THE PERIODIC LAW

It is seen from the examples given in the preceding chapters that the sum of the data concerning the chemical transformations proper to the elements is insufficient for accurately judging the resemblance of the elements, inasmuch as this resemblance may be many-sided. Thus, lithium or barium are in certain respects analogous to sodium or potassium, and in others to magnesium or calcium. It is evident, therefore, that for a true judgment it is necessary to have exact and measurable indices.

Among these exactly measurable and common properties or indices of the elements, or of their corresponding compounds, belong: (*a*) isomorphism, or the analogy of crystalline forms, and, connected with it, the power to form crystalline mixtures which are isomorphous; (*b*) the relation of the volumes of analogous compounds of the elements; (*c*) the composition of their saline compounds; and (*d*) the relation of the atomic weights of the elements. In this chapter we shall briefly consider these four aspects of the matter, which are exceedingly important for a right grouping of the elements, for facilitating their investigation, as well as for judging of their most important properties.

Historically the first, and an important and convincing, method for finding a resemblance between the compounds of two different elements is by *isomorphism*. This conception was introduced into chemistry by Mitscherlich (in 1820), who demonstrated that the corresponding salts of arsenic acid, H_3AsO_4, and phosphoric acid, H_3PO_4, crystallise with an equal quantity of water, show an exceedingly close resemblance

in crystalline form (as regards the angles of their faces and axes), and are able to crystallise together from solutions in the same crystals containing a mixture of the isomorphous compounds. Isomorphous substances are those which, with an equal number of atoms in their molecules, present an analogy in their chemical reactions, a close resemblance in their properties, and a similar or very nearly similar crystalline form ; they often contain certain elements in common, from which it is concluded that the remaining (different) elements are analogous to each other. And inasmuch as crystalline forms are subject to exact measurement, therefore the external form, or the relation of the molecules which causes their grouping into crystalline forms, is seen to be as great a help for judging the internal forces acting between the atoms as a comparison of reactions, vapour densities, and other like relations. We have already seen examples of this in the preceding pages. It will be sufficient to recall to mind that the compounds of the alkali metals with the halogens RX, in a crystalline form, all belong to the cubic system and crystallise in octahedra or cubes—for example, sodium chloride, potassium chloride, potassium iodide, rubidium chloride, &c. The nitrates of rubidium and cæsium appear in anhydrous crystals of the same form as potassium nitrate. The carbonates of the metals of the alkaline earths are isomorphous with calcium carbonate—that is, they either appear in forms like calc spar or in the rhombic system in crystals analogous to aragonite.[1] Furthermore, sodium nitrate crystallises in rhombohedra, closely resembling the rhombohedra of calc spar (calcium carbonate), $CaCO_3$, whilst potassium nitrate appears in the form of aragonite, $CaCO_3$, and the number of atoms in both kinds of salts is analogous ; they contain one atom of a metal (K, Na, Ca), one atom of a non-metal (C, N), and three atoms of oxygen. The analogy of form evidently coincides with the analogy of atomic composition. But, as we have learnt from the previous description of these salts, there is not any close resemblance in their properties. It is evident that calcium carbonate approaches more nearly to magnesium carbonate than to sodium nitrate, although their crystalline forms are equally alike. Isomorphous substances which are perfectly analogous to each other are not only characterised by a close resemblance of forms (homeomorphism), but also by the

[1] The crystalline forms of aragonite, strontianite, and witherite belong to the rhombic system; the angle of the prism of $CaCO_3$ is 116° 10′, of $SrCO_3$ 117° 19′, and of $BaCO_3$ 118° 30′. On the other hand, the crystalline forms of calc spar, magnesite, and calamine, which resemble each other quite as closely, belong to the rhombohedral system, with the angle of the rhombohedra for $CaCO_3$ 105° 8′, $MgCO_3$ 107° 10′, and $ZnCO_3$ 107° 40′. From this comparison it is already evident that zinc is more closely allied to magnesium than magnesium to calcium.

faculty of entering into analogous reactions, which is not the case with RNO_3 and RCO_3. The most important and direct method of judging perfect isomorphism—that is, the positive analogy of two compounds—is given by that property according to which analogous compounds are able to separate from solutions *in homogeneous crystals, containing the most varied quantitative proportions* of the analogous substances which enter into their composition. These quantities do not seem to be in dependence on the molecular or atomic weights, and if they are governed by any laws they must be analogous to those which refer to indefinite chemical compounds.[2] This will be clear from the following examples. Potassium chloride and potassium nitrate are not isomorphous with each other, and are in an atomic relation composed in a different manner. If these salts be mixed in a solution and the solution be evaporated, then individual crystals of each of these salts will separate in that crystalline form which is proper to each of them. The crystals will not contain a mixture of the two salts. But if we mix the solutions of two isomorphous salts together, then, under certain circumstances, crystals will be obtained which contain both these substances. However, this cannot be taken as an absolute rule. Thus, if we take a solution saturated at a high temperature with a mixture of potassium and sodium chlorides, then on evaporation sodium chloride only will separate, and on cooling only potassium chloride. The first will contain a very little potassium chloride, and the latter very little sodium chloride.[3] But if we take, for example, a mixture of solutions of magnesium sulphate and of zinc sulphate, then they cannot be separated from each other by evaporating the mixture, notwithstanding the rather considerable difference in the solubility of

[2] Solutions form the commonest examples of indefinite chemical compounds. But the isomorphous mixtures which are so common among the crystalline compounds of silica forming the crust of the earth, as well as alloys, which are so important in the application of metals to the arts, are also instances of indefinite compounds. And if in Chapter I., and in many other portions of this work, it has been proved necessary to admit the presence of definite compounds (in a state of dissociation) in solutions, then the same refers with even greater force to isomorphous mixtures and alloys. For this reason in many places in this work I turn to facts which compel us to recognise the existence of definite chemical compounds in all isomorphous mixtures and alloys.

[3] The cause of the difference which is observed in different compounds of the same type, with respect to their property of forming isomorphous mixtures, must not be looked for in the difference of their volumetric composition, as many, including Kopp, affirm. The molecular volumes (found by dividing the molecular weight by the density) of those isomorphous substances which do give intermixtures are not nearer to each other than the volumes of those which do not give mixtures; for example, for magnesium carbonate the combining weight is 84, density 3·06, and volume 27; for calcium carbonate in the form of calc spar the volume = 37, and in the form of aragonite 33; for strontium carbonate = 41, for barium carbonate = 46; that is, the volume of these closely-allied isomorphous substances increases with the combining weight. The same is observed if

these salts. Again, the isomorphous salts, magnesium carbonate and calcium carbonate, are found together—that is, in one crystal—in nature. The angle of the rhombohedron of these magnesia-lime spars is intermediate between the angles proper to both spars individually (for calcium carbonate, the angle of the rhombohedron, is 105° 8′ ; magnesium carbonate, 107° 30′ ; $CaMg(CO_3)_2$, 106° 10′). Certain of these *isomorphous mixtures* of calc and magnesia spars appear in well-formed crystals, and in this case there not unfrequently exists a simple molecular proportion of strictly definite chemical combination between the component salts—for instance, $CaCO_3,MgCO_3$—whilst in other cases, especially in the absence of distinct crystallisation (in dolomites), no such simple molecular proportion is observable; this is also the case in many artificially prepared isomorphous mixtures. The microscopical researches (and optical, especially those as regards the rotation of the plane of polarisation) of Professor Inostrantzoff and others, show that in many cases there is really a mechanical, although microscopically minute, juxtaposition in one whole of the heterogeneous crystals of calcium carbonate (double refracting) and of the compound $CaMgC_2O_6$. If we suppose the adjacent parts to be microscopically small (on the basis of the researches of Mallard, Wernhoff, and others), we obtain an idea of isomorphous mixtures. A formula of the following kind is given to isomorphous mixtures: for instance, for spars, RCO_3, where R= Mg,Ca, and where it may be Fe,Mn . . . ., &c. This means that the Ca is partially replaced by Mg or another metal. Alums form a common example of the separation of isomorphous mixtures from solutions. They are double sulphates (or seleniates) of alumina (or oxides isomorphous with it) and the alkalis, which crystallise in well-formed crystals. If aluminium sulphate be mixed with potassium sulphate, then an alum separates, having the composition $KAlS_2O_8,12H_2O$. If sodium sulphate or ammonium sulphate, or rubidium (or thallium) sulphate, be used, we obtain alums having the composition $RAlS_2O_8,12H_2O$. They all not only crystallise in the cubic system, but also contain an equal atomic quantity of water of crystallisation ($12H_2O$). Besides which, if we mix solutions of the potassium and ammonium ($NH_4AlS_2O_3,12H_2O$) alums together, then the crystals

we compare sodium chloride (molecular volume =27) with potassium chloride (volume =37), or sodium sulphate (volume =55) with potassium sulphate (volume = 66), or sodium nitrate =39 with potassium nitrate =48, although the latter are less capable of giving isomorphous mixtures than the former. It is evident that the cause of isomorphism cannot be explained by an approximation in molecular volumes. It is more likely that, given a similarity in form and composition, the faculty to give isomorphous mixtures is connected with he aws and degree of solubility.

which separate will contain different proportions of the alkalis taken, and separate crystals of the alums of one or the other kind will not be obtained, but each separate crystal will contain both potassium and ammonium. Nor is this all; if we take a crystal of a potassium alum and immerse it in a solution capable of yielding ammonia alum, then the crystal of the potash alum will continue to grow and increase in size in this solution—that is, a layer of the ammonia or other alum will deposit itself upon the planes bounding the crystal of the potash alum. This is very distinctly seen if a colourless crystal of a common alum be immersed in a saturated violet solution of chrome alum, $KCrS_2O_8,12H_2O$, which then deposits itself in a violet layer over the colourless crystal of the alumina alum, as was observed even before Mitscherlich noticed it. If this crystal be then immersed in a solution of an alumina alum, a layer of this salt will form over the layer of chrome alum, so that one alum is able to incite the growth of the other. If the deposition proceed simultaneously, the resultant intermixture may be minute and indivisible, but its nature is understood from the preceding experiments; the attractive force of crystallisation of isomorphous substances is so nearly equal that the attractive power of an isomorphous substance induces a crystalline superstructure exactly the same as the attractive force of like crystalline particles. From this it is evident that one isomorphous substance may *induce the crystallisation*[4] of another. Such a phenomenon explains, on the one hand, the aggregation of different isomorphous substances in one crystal, whilst, on the other hand, it serves as a most exact indication of the nearness both of the molecular composition of isomorphous substances and of these forces which are proper to the elements which distinguish the isomorphous substances. Thus, for example, ferrous sulphate or green vitriol crystallises in the monoclinic system and contains seven molecules of water, $FeSO_4,7H_2O$, whilst copper vitriol crystallises with five molecules of water in the triclinic system, $CuSO_4,5H_2O$; nevertheless, it may be easily proved that both salts are perfectly isomorphous, that they are able to appear in identically the same forms and with an equal molecular amount of water. For instance, Marignac, by evaporating a mixture of sulphuric acid and ferrous sulphate under the receiver of an air-pump, first obtained crystals of the hepta-hydrated salt and then of the penta-hydrated salt $FeSO_4,5H_2O$, which were perfectly similar to the crystals of copper sulphate. Furthermore, Lecoq de Boisbaudran, by immersing crystals of $FeSO_4,7H_2O$ in a supersaturated solution of copper sulphate,

[4] A phenomenon of a like kind is shown for magnesium sulphate in Note 27 of the last chapter. In the same example we see what a complication the phenomena of dimorphism may introduce into the matter of comparing the forms of analogous compounds.

caused the latter to deposit in the same form as ferrous sulphate, in crystals of the monoclinic system, $CuSO_4,7H_2O$.

Hence it is evident that isomorphism—that is, the analogy of forms and the faculty to provoke crystallisation—may serve as a means for the discovery of analogies in molecular composition. We will take an example in order to render this clear. If, instead of aluminium sulphate, we add magnesium sulphate to potassium sulphate, then, on evaporating the solution, the double salt $K_2MgS_2O_8,6H_2O$ separates instead of an alum, and in it the ratio of the component parts (in alums one atom of potassium per $2SO_4$, and here two atoms) and the amount of water of crystallisation (in alums 12 and here 6 equivalents per $2SO_4$) are quite different from what they are in alums; nor is this double salt in any way isomorphous with the alums, or capable of forming an isomorphous crystalline mixture with them, nor does the one salt provoke the crystallisation of the other. From this we must conclude that although alumina and magnesia, or aluminium and magnesium, resemble each other, they are not isomorphous, and that, although they give partially similar double salts, these salts are not analogous to each other. And this is expressed in their chemical formulæ by the fact that the number of atoms in alumina or aluminium oxide, Al_2O_3, is different from the number in magnesia, MgO. Aluminium is trivalent and magnesium bivalent. Thus, having obtained a double salt from a given metal, it is possible to judge of the analogy of the given metal with aluminium or with magnesium, or of the absence of such an analogy, from the composition and form of this salt. Thus zinc, for example, does not form alums, but forms a double salt with potassium sulphate, which has a composition exactly like that of the corresponding salt of magnesium. It is often possible to distinguish the bivalent metals analogous to magnesium or calcium from the trivalent metals, like aluminium, by a similar method. Furthermore, the specific heat and vapour density serve as guides. There are also indirect proofs. Thus iron gives ferrous compounds, FeX_2, which are isomorphous with the compounds of magnesium, and ferric compounds, FeX_3, which are isomorphous with the compounds of aluminium; and, in this instance, the relative composition is directly determined by analysis, because, for a given amount of iron, $FeCl_2$ only contains two-thirds of the amount of chlorine which occurs in $FeCl_3$.

Thus in the building up of like molecules in crystalline forms we see one of the numerous means for judging of the internal world of molecules and atoms, and one of the weapons for conquests in the invisible world of molecular mechanics which forms the main object of

physico-chemical knowledge. This weapon [5] has more than once been employed for discovering the analogy of elements and of their compounds.

[5] The property of solids of occurring in regular crystalline forms—the occurrence of many substances in the earth's crust in these forms—and those geometrical and simple laws which govern the formation of crystals, have long ago attracted the attention of the naturalist to crystals. The crystalline form is, without doubt, the expression of the relation in which the atoms occur in the molecules, and the molecules in the mass of a substance. Crystallisation is determined by the distribution of the molecules along the direction of the greatest cohesion, and therefore those forces must take part in the crystalline distribution of matter which act between the molecules; and, as they depend on the forces binding the atoms together in the molecules, therefore a very close connection must exist between the atomic composition and the distribution of the atoms in the molecule on the one hand, and with the crystalline forms of substances on the other hand, and hence an insight into the composition may be arrived at from the crystalline form. Such is the elementary and *a priori* idea which lies at the base of all researches into *the connection between composition and crystalline form.* Haüy, in 1811, established the following fundamental law, which has been worked out by later investigators: That the fundamental crystalline form for a given chemical compound is constant (varies only in combinations), and that with a change of composition the crystalline form also changes, naturally with the exception of such limiting forms as the cube, regular octahedron, &c., which may belong to various substances of the regular system. The fundamental form is determined by the angles of certain fundamental forms (prisms, pyramids, rhombohedra), or the ratio of the crystalline axis, and is connected with the optical and many other properties of crystals. Since the establishment of this law the description of definite compounds in a solid state is accompanied by a description (measurement) of its crystals, which forms an invariable, distinct, and measurable index. The most important epochs in the further history of this question were formed by the following discoveries:—Klaproth, Vauquelin, and others showed that aragonite has the same composition as calc spar, whilst the former belongs to the rhombic and the latter to the hexagonal system. Haüy at first considered that the composition, and after that the structure, of the atoms in the molecules was different. But at present no difference in the reactions of the two varieties of calcium carbonate is known, although it cannot be positively stated that none exists (very few researches have been made in this direction). Beudant, Frankenheim, Laurent, and others found that the forms of the two nitres, KNO_3 and $NaNO_3$, exactly correspond with the forms of aragonite and calc spar; that they are able, moreover, to pass from one form into another, and that the difference of the forms is accompanied by a small alteration of the angles, because the angle of the prisms of potassium nitrate and aragonite is 119° and of sodium nitrate and calc spar, 120°; and therefore dimorphism, or the crystallisation of one substance in different forms, does not essentially provoke a great alteration in the distribution of the molecules, although it clearly exists. The researches of Mitscherlich (1822) on the dimorphism of sulphur confirmed this conclusion, although it cannot yet be affirmed that in dimorphism the arrangement of the atoms remains unaltered, and that only the molecules are distributed differently. Leblanc, Berthier, Wollaston, and others, already knew that many substances of different composition appear in the same forms, and crystallise together in one crystal. Gay-Lussac (1816) showed that crystals of potash alum continue to grow in a solution of ammonia alum. Beudant (1817) explained this phenomenon by the *assimilation* of a foreign substance by a substance having a great force of crystallisation, which he confirmed by many natural and artificial examples. But Mitscherlich, and afterwards Berzelius and Henry Rose and others, showed that such an assimilation only exists with a similarity or nearness of the forms of the individual substances, and with a certain degree of chemical analogy. Thus was established the idea of *isomorphism*, as an analogy of forms by reason of a resemblance of atomic composition,

The regularity and simplicity expressed by the exact laws of crystalline form repeat themselves in the aggregation of the atoms to form molecules. Here, as there, there are but few forms which are essen-

and by it was explained the variability of the composition of a number of minerals as isomorphous mixtures. Thus all the garnets are expressed by the general formula: $(RO)_3M_2O_3(SiO_2)_3$, where R = Ca, Mg, Fe, Mn, and M = Fe, Al, and where we may have either R and M separately, or their equivalent compounds, or their mixtures in all possible proportions.

But other facts, which render the correlation of form and composition still more complex, have accumulated side by side with a mass of data which may be accounted for by admitting the conceptions of isomorphism and dimorphism. Foremost among the former stand the phenomena of *homeomorphism*—that is, a nearness of forms with a difference of composition—and then the cases of polymorphism and hemimorphism—that is, a nearness of the fundamental forms or only of certain angles for substances which are near or analogous in their composition. Instances of homeomorphism are very numerous. Many, however, may be reduced to a resemblance of atomic composition, although they do not correspond to an isomorphism of the component elements; for example, CdS (greenockite) and AgI, $CaCO_3$ (aragonite) and KNO_3, $CaCO_3$ and $NaNO_3$, $BaSO_4$ (heavy spar), $KMnO_4$ (potassium permanganate), and $KClO_4$ (potassium perchlorate), Al_2O_5 (corundum) and $FeTiO_3$ (titanic iron ore), FeS_2 (marcasite, rhombic system) and FeSAs (arsenical pyrites), NiS and NiAs, &c. But besides these instances there are homeomorphous substances with an absolute dissimilarity of composition. Many such instances were pointed out by Dana. Cinnabar, HgS, and susannite, $PbSO_4 3PbCO_5$, appear in very analogous crystalline forms; the acid potassium sulphate crystallises in the monoclinic system in crystals analogous to felspar, $KAlSi_3O_8$; glauberite, $Na_2Ca(SO_4)_2$, augite, $RSiO_3$ (R = Ca, Mg), sodium carbonate, $Na_2CO_3,10H_2O$, glauber salt, $Na_2SO_4,10H_2O$, and borax $Na_2BrO_7,10H_2O$, not only belong to the same system (monoclinic) but exhibit an analogy of combinations and a nearness of corresponding angles. These and many other similar cases might appear to be perfectly arbitrary (especially as a *nearness* of angles and fundamental forms is a relative idea) were there not other cases where a resemblance of properties and a distinct relation in the variation of composition is connected with a resemblance of form. Thus, for example, alumina, Al_2O_3, and water, H_2O, are frequently found in many pyroxenes and amphiboles which only contain silica and magnesia (MgO, CaO, FeO, MnO). Scheerer and Hermann, and many others, endeavoured to explain such instances by *polymeric isomorphism*, stating that MgO may be replaced by $3H_2O$ (for example, olivine and serpentine), SiO_2 by Al_2O_3 (in the amphiboles, talcs), and so on. A certain number of the instances of this order are subject to doubt, because many of the natural minerals which served as the basis for the establishment of polymeric isomorphism in all probability no longer present their original composition but one which has been altered under the influence of solutions which have come into contact with them, and which therefore belong to the class of *pseudomorphs*, or false crystals. There is, however, no doubt of the existence of a whole series of natural and artificial homeomorphs, which differ from each other by atomic amounts of water, silicas, and some other components parts. Thus, Thomsen (1874) showed a very striking instance. The metallic chlorides, RCl_2, often crystallise with water, and then they do not contain less than one molecule of water per atom of chlorine. The most familiar representative of the order $RCl_2,2H_2O$ is $BaCl_2,2H_2O$, which crystallises in the rhombic system. Barium bromide, $BaBr_2,2H_2O$, and copper chloride, $CuCl_2,2H_2O$, have nearly the same forms; potassium iodate, KIO_4; potassium chlorate, $KClO_4$; potassium permanganate, $KMnO_4$; barium sulphate, $BaSO_4$; calcium sulphate, $CaSO_4$; sodium sulphate, Na_2SO_4; barium formate, $BaC_2H_2O_4$, and others, have almost the same crystalline form (of the rhombic system). Parallel to this series is that of the metallic chlorides containing $RCl_2,4H_2O$, of the sulphates of the composition $RSO_4,2H_2O$, and the formates $RC_2H_2O_4,2H_2O$. These compounds belong to the monoclinic system, have a close resemblance of form, and

tially different, and their observed diversity reduces itself into a few fundamental differences. There, the molecules aggregate themselves

differ from the first series by containing two more molecules of water. The addition of two more molecules of water in all the above series also gives forms of the monoclinic system closely resembling each other; for example, $NiCl_2,6H_2O$ and $MnSO_4,4H_2O$. Hence we see that not only is $RCl_2,2H_2O$ analogous in form to RSO_4 and $RC_2H_2O_4$, but that their compounds with $2H_2O$ and with $4H_2O$ also exhibit closely analogous forms. If we take away the elements R and O_2 common to all these compounds, it appears that the form remains unchanged, with the substitution of Cl_2H_2 by SO_2 and $C_2H_2O_2$. An example of homeomorphism among the chlorides is also seen in the close resemblance of the forms of the hexagonal hydrated chlorides of calcium and strontium, and of the double chlorides. Thus, in $CaCl_2,6H_2O$ and $SrCl_2,6H_2O$ the ratio of the vertical to the horizontal axis is as 0·496 : 1, and as 0·508 : 1, and the angle of the rhombohedra = 129° 1′ and 128° 2′; and in such compounds as $NiPtCl_6,6H_2O$, $MgSnF_6,6H_2O$, $ZnSnF_6,H_2O$, &c., the ratio of the axes is from 0·508 to 0·519 : 1, and the angle of the rhombohedra from 127° to 128° 17′. From these examples it is evident that the conditions which determine a given form may be repeated not only in the presence of an isomorphous exchange—that is, with an equal number of atoms in the molecule—but also in the presence of an unequal number when there are peculiar and as yet ungeneralised relations in composition. Thus, ZnO and Al_2O_3 exhibit a close analogy of form. Both oxides belong to the rhombohedral system, and the angle between the pyramid and the terminal plane of the first is 118° 7′ and of the second 118° 49′. Alumina, Al_2O_3, is also analogous in form to SiO_2, and we shall see that these analogies of form are conjoined with a certain analogy in properties. It is not surprising, therefore, that in the complex molecule of a siliceous compound it is sometimes possible to replace SiO_2 by means of Al_2O_3, as Scheerer admits. The oxides Cu_2O, MgO, NiO, Fe_3O_4, CeO_2, crystallise in the regular system, although they are of very different atomic structure. Marignac demonstrated the perfect analogy of the forms of K_2ZrF_6 and $CaCO_3$, and the former is even dimorphous, like the calcium carbonate. The same salt is isomorphous with R_2NbOF_5 and $R_2WO_2F_4$, where R is an alkali metal. There is an equivalency between $CaCO_3$ and K_2ZrF_6, because K_2 is equivalent to Ca, C to Zr, and F_6 to O_3, and with the isomorphism of the other two salts we find besides an equal contents of the alkali metal—an equal number of atoms on the one hand and an analogy to the properties of K_2ZrF_6 on the other. The long-known isomorphism of the corresponding compounds of potassium and ammonium, KX and NH_4X, may be taken as the simplest example of the fact that an analogy of form shows itself with an analogy of chemical reaction even without an equality in atomic composition. Therefore the ultimate progress of the entire doctrine of the correlation of composition and crystalline forms will only be arrived at with the accumulation of a sufficient number of facts collected on a plan corresponding with the problems which here present themselves. The first steps have already been made. The researches of the Geneva savant, Marignac, on the crystalline form and composition of many of the double fluorides, and the work of Wyruboff on the ferricyanides and other compounds, are particularly important in this respect. It is already evident that, with a definite change of composition, certain angles remain constant, notwithstanding that others are subject to a great alteration. Such an instance of the relation of forms was observed by Laurent, and named *hemimorphism* (an anomalous term) by him when the analogy is limited to certain angles, and *paramorphism* when the forms in general approach each other but belong to different systems. So, for example, the angle of the planes of a rhombohedra may be greater or less than 90°, and therefore such acute and obtuse rhombohedra may approach very near to the cube. Hausmannite, Mn_3O_4, belongs to the tetragonal system, and the planes of its pyramid are inclined at an angle of about 118°, whilst magnetic iron ore, Fe_3O_4, which resembles hausmannite in many respects, appears in regular octahedra—that is, pyramidal planes are inclined at an angle of 109° 28′. This is an example of paramorphism; the systems are different, the composi-

into crystalline forms; here, the atoms aggregate themselves into molecular forms or into *the types of compounds*. Here as there, the fundamental crystalline or molecular forms are liable to variations, conjunctions, and combinations. If we know that potassium gives compounds of the fundamental type KX, where X is a univalent element (which combines with one atom of hydrogen, and is, according to the law of substitution, able to replace it), then we know the composition of its compounds: K_2O, KHO, KCl, NH_2K, KNO_3, K_2SO_4, $KHSO_4$, $K_4Mg(SO_4)_2$, $6H_2O$, &c. All the possible derivative crystalline forms are not known. So also all the atomic combinations are not known for every element. In the case of potassium, KCH_3, K_3P, K_4Pt, and other like compounds which exist for hydrogen or chlorine, are unknown.

Only a few fundamental types exist for the building up of atoms into molecules, and the majority of them are already known to us. If X stand for a univalent element, and R for an element combined with it, then eight atomic types may be observed—

$$RX,\ RX_2,\ RX_3,\ RX_4,\ RX_5,\ RX_6,\ RX_7,\ RX_8.$$

Let X be chlorine or hydrogen. Then as examples of the first type we have: H_2, Cl_2, HCl, KCl, NaCl, &c. The compounds of oxygen or calcium may serve as examples of the type RX_2 : OH_2, OCl_2, OHCl,

tions are analogous, and there is a certain resemblance in form. Hemimorphism has been found in many instances of saline and other substitutions. Thus, Laurent demonstrated, and Hintze confirmed (1878), that naphthalene derivatives of analogous composition are hemimorphous. Nicklès (1849) showed that in ethylene sulphate the angle of the prism is 125° 26′, and in the nitrate of the same radicle 126° 95′. The angle of the prism of methylamine oxalate is 131° 20′, and of fluoride, which is very different in composition from the former, the angle is 132°. Groth (1870) endeavoured to indicate in general what kinds of change of form proceeds with the substitution of hydrogen by various other elements and groups, and he observed a regularity which he termed *morphotropy*. The following examples show that motphotropy recalls the hemimorphism of Laurent. Benzene, C_6H_6, rhombic system, ratio of axis 0·891 : 1 : 0·799. Phenol, $C_6H_5(OH)$, and resorcinol, $C_6H_4(OH)_2$, also rhombic system, but the ratio of one axis is changed—thus, in resorcinol, 0·910 : 1 : 0·540; that is, a portion of the crystalline structure in one direction is the same, but in the other direction it is changed, whilst in the rhombic system dinitrophenol, $C_6H_3(NO_2)_2(OH) = 0·833 : 1 : 0·753$; trinitrophenol (picric acid), $C_6H_2(NO)_5(OH) = 0·937 : 1 : 0·974$; and the potassium salt = 0·942 : 1 : 1·354. Here the ratio of the first axis is preserved—that is, certain angles remain constant. Laurent likens hemimorphism to architectural style. Thus, Gothic cathedrals differ in many respects, but there is an analogy expressed both in the sum total of their common relations and in certain details. It is evident that we may expect many fruitful results for molecular mechanics (which forms a problem common to many provinces of natural science) from the further working out of the data concerning those variations which take place in crystalline form when the composition of a substance is subjected to a known change, and therefore I consider it useful to the young scientific man seeking for matter for independent scientific research to point out this vast field for work which is presented by the correlation of form and composition. The geometrical regularity and varied beauty of crystalline forms offer no small attraction to research of this kind.

CaO, $Ca(OH)_2$, $CaCl_2$, &c. For the third type RX_3 we know the representative NH_3 and the corresponding compounds N_2O_3, NO(OH), NO(OK), PCl_3, P_2O_3, PH_3, SbH_3, Sb_2O_3, B_2O_3, BCl_3, Al_2O_3, &c. The type RX_4 is known among the hydrogen compounds. Marsh gas, CH_4, and its corresponding saturated hydrocarbons, C_nH_{2n+2}, are the best representatives. Also CH_3Cl, CCl_4, $SiCl_4$, $SnCl_4$, SnO_2, CO_2, SiO_2, and a whole series of other compounds come under this class. The type RX_5 is also already familiar to us, but there are no purely hydrogen compounds among its representatives. Sal-ammoniac, NH_4Cl, and the corresponding $NH_4(OH)$, $NO_2(OH)$, $ClO_2(OK)$, as well as PCl_5, $POCl_3$, &c., are representatives of this type. In the higher types also there are no hydrogen compounds, but in the type RX_6 there is the chlorine compound WCl_6. However, there are many oxygen compounds, and among them SO_3 is the best known representative. To this class also belong $SO_2(OH)_2$, SO_2Cl_2, $SO_2(OH)Cl$, CrO_3, &c., all of an acid character. In general of the higher types there are only oxygen and acid representatives. The type RX_7 we know in perchloric acid, $ClO_3(OH)$, and potassium permanganate, $MnO_3(OK)$, is also a member. The type RX_8 is very rare, osmic anhydride, OsO_4, is the best known representative of it. The still more complex combinations—which are so clearly expressed in the crystallo-hydrates, double salts and like compounds—although they may be regarded as independent, are, however, most easily understood with our present store of knowledge as aggregations of whole molecules to which there are no corresponding double compounds, containing one atom of an element R and many atoms of other elements RX_n. The above types embrace all cases of direct combinations of atoms, and the formula $MgSO_4,7H_2O$ cannot, without doing violence to known facts, be directly deduced from the types MgX_n or SX_n, whilst the formula $MgSO_4$ corresponds both with the type of the magnesium compounds MgX_2 and with the type of the sulphur compounds SO_2X_2, or in general SX_6, where X_2 is replaced by $(OH)_2$, with the substitution in this case of H_2 by the atom Mg, which always replaces H_2.[6]

[6] However, one cannot but remark that the sodium crystallo-hydrates often contain $10H_2O$, the magnesium crystallo-hydates 6 and $7H_2O$, and that the type PtM_2X_6 is proper to the double salts of platinum, &c. With the further development of our knowledge concerning crystallo-hydrates, double salts, alloys, solutions, &c., in the *chemical sense* of feeble compounds (that is, such as are easily destroyed by feeble chemical influences) it will probably be possible to arrive at a perfect generalisation for them. For the present these subjects have only been studied by the way or by chance, our knowledge of them is accidental and destitute of system, and therefore it is impossible to expect as yet any generalisation as to their nature. The days of Gerhardt are not long past when only three types were recognised: RX, RX_2, and RX_3; the type RX_4 was afterwards added (by Cooper, Kekulé, Butleroff, and others), mainly for the purpose of generalising

The four lower types RX, RX_2, RX_3, and RX_4 are met with in compounds of the elements R with chlorine and oxygen, and also in their compounds with hydrogen, whilst the four higher types only appear for such acid compounds as are formed by chlorine, oxygen, and like elements.

Among the oxygen compounds, the *saline oxides* which are capable of forming salts either through the function of a base or through the function of an acid anhydride attract the greatest interest in every respect. Certain elements, like calcium and magnesium, only give one saline oxide—for example, MgO, corresponding with the type MgX_2. But the majority of the elements appear in several such forms. Thus copper gives CuX and CuX_2, or Cu_2O and CuO. If an element R gives a higher type RX_n, then there often also exist, as if by symmetry, lower types RX_{n-2}, RX_{n-4}, and in general such which differ from the type RX_n by an even number of X. Thus in the case of sulphur the types SX_2, SX_4, and SX_6 are known—for example SH_2, SO_2, and SO_3. The last type is the highest SX_6. The types SX_5 and SX_3 do not exist. But even and uneven types sometimes appear for one and the same element. Thus the types RX and RX_2 are known for copper and mercury.

Among the *saline* oxides only the *eight types* enumerated below are known to exist. They determine the possible formulæ of the compounds of the elements, if it be taken into consideration that an element which gives a certain type of combination may also give lower types. For this reason the rare type of the *suboxides* or quaternary oxides R_4O (for instance, Ag_4O, Ag_4Cl) is not characteristic; it is always accompanied by one of the higher grades of oxidation, and the compounds of this type are distinguished by their great chemical instability, and split up into an element and the higher compound (for instance, $Ag_4O = 2Ag + Ag_2O$). Many elements beside this form transition oxides whose composition is intermediate, and which are

the data respecting the carbon compounds. And indeed many are still satisfied with these types, and derive the higher types from them—for instance, RX_5 from RX_3, as, for example, $POCl_3$ from PCl_3, considering the oxygen to be bound both to the chlorine (as in $HClO$) and to the phosphorus. But the time has now arrived when it is clearly seen that the forms RX, RX_2, RX_3, and RX_4 do not exhaust the whole variety of phenomena. The revolution became evident when Würtz showed that PCl_5 is not a compound of $PCl_3 + Cl_2$, although it may decompose into them, but a whole molecule capable of passing into vapour, PCl_5 like PF_5 and SiF_4. But in my opinion the time will come for the recognition of types still higher than RX_5. In confirmation of this opinion I cite certain facts in the further exposition of this work. Oxalic acid, $C_2H_2O_4$, gives a crystallo-hydrate with $2H_2O$, but it may be referred to the type CH_4, or rather to the type of ethane, C_2H_6, in which all the atoms of hydrogen are replaced by hydroxyl, $C_2H_2O_4 2H_2O = C_2(OH)_6$.

able, like N_2O_4, to split up into the lower and higher oxides. Thus iron gives magnetic oxide, Fe_3O_4, which is in all respects (by its reactions) a compound of the suboxide FeO with the oxide Fe_2O_3. The independent and more or less stable saline compounds correspond with the following eight types :—

R_2O ; salts RX, hydroxides ROH. Generally basic like K_2O, Na_2O, Hg_2O, Ag_2O, Cu_2O ; if there are acid oxides of this composition they are very rare, are only formed by distinctly acid elements, and even then have only feeble acid properties ; for example, Cl_2O.

R_2O_2 or RO ; salts RX_2, hydroxides $R(OH)_2$. The most simple basic salts R_2OX_2 or R(OH)X ; also an almost exclusively basic type, but the basic properties are more feebly developed than in the preceding type. For example, CaO, MgO, BaO, PbO, FeO, MnO, &c.

R_2O_3 ; salts RX_3, hydroxides $R(OH)_3$, RO(OH), the most simple basic salts ROX, $R(OH)X_2$. The bases are unenergetic, like Al_2O_3, Fe_2O_3, Tl_2O_3, Sb_2O_3. The acid properties are also feebly developed ; for instance, in B_2O_3, but with the non-metals the properties of acids are already clear, for instance P_2O_3, $P(OH)_3$.

R_2O_4 or RO_2 ; salts RX_4 or ROX_2, hydroxides $R(OH)_4$, $RO(OH)_2$. Rarely bases (feeble), like ZrO_2, PtO_2 ; more often acid oxides, but the acid properties are in general feeble, as in CO_2, SO_2, SnO_2. Many intermediate oxides appear in this and the preceding and the following types.

R_2O_5 ; salts principally of the types ROX_3, RO_2X, $RO(OH)_3$, $RO_2(OH)$ rarely RX_5. The basic character (X, a halogen, simple or complex—for instance, NO_3, Cl, &c.) is feeble ; the acid character predominates, as is seen in N_2O_5, P_2O_5, Cl_2O_5 ; then X=OH, OK, &c., for example $NO_2(OK)$.

R_2O_6 or RO_3 ; salts and hydroxides generally of the type RO_2X_2, $RO_2(OH)_2$. Oxides of an acid character, as SO_3, CrO_3, MnO_3. Basic properties rare and feebly developed as in UO_3.

R_2O_7 ; salts of the form RO_3X, $RO_3(OH)$, acid oxides—for instance, Cl_2O_7, Mn_2O_7. Basic properties as feebly developed as the acid properties in the oxides R_2O.

R_2O_8 or RO_4. A very rare type, and only known in OsO_4 and RuO_4.

It is evident from the circumstance that in all the higher types the *acid hydroxides* and salts with one atom of an element contain, like the higher saline type RO_4, *not more than four atoms of oxygen*, that the formation of the saline oxides is governed by a certain common principle which is best looked for in the properties of oxygen itself. The hydrate of the oxide RO_2 is of the higher type $RO_2 2H_2O$=

$RH_4O_4 = R(HO)_4$. Such, for example, is the hydrate of silica and the salts (orthosilicates) corresponding with it, $Si(MO)_4$. The oxide R_2O_5 corresponds with the hydrate $R_2O_5 3H_2O = 2RH_3O_4 = 2RO(OH)_3$. Such is orthophosphoric acid PH_3O_3. The hydrate of the oxide RO_3 is $RO_3H_2O = RH_2O_4 = RO_2(OH)_2$—for instance, sulphuric acid. The hydrate corresponding to R_2O_7 is evidently $RHO_4 = RO_3(OH)$—for example, perchloric acid. Here, besides containing O_4, it must further be remarked that *the amount of hydrogen in the hydrate is equal to the amount of hydrogen in the hydrogen compound.* Thus silicon give SiH_4 and SiH_4O_4, phosphorus PH_3 and PH_3O_4, sulphur SH_2 and SH_2O_4, chlorine ClH and $ClHO_4$. This, if it does not explain, at least connects in a harmonious and general system the fact that *the elements are capable of combining with a greater amount of oxygen, the less the amount of hydrogen which they are able to retain.* In this the key to the comprehension of all further deductions must be looked for, and therefore we will formulate this rule in general terms. An element R gives a hydrogen compound RH_n, the hydrate of its higher oxide will be RH_nO_4, and therefore the higher oxide will contain $2RH_nO_4 - nH_2O = R_2O_{8-n}$. For example, chlorine gives ClH, hydrate $ClHO_4$, and the higher oxide Cl_2O_7. Thus carbon gives CH_4 and CO_2. So also, SiO_2 and SiH_4 are the higher compounds of silicon with hydrogen and oxygen, like CO_2 and CH_4. Here the amounts of oxygen and hydrogen are equivalent. Nitrogen combines with a large amount of oxygen, forming N_2O_5, but on the other hand with a small quantity of hydrogen in NH_3. *The sum of the equivalents of hydrogen and oxygen,* occurring in combination with an atom of nitrogen, is, as always in the higher types, equal to *eight.* It is the same with the other elements which combine with hydrogen and oxygen. Thus sulphur gives SO_3; consequently, six equivalents of oxygen fall to an atom of sulphur, and in SH_2 two equivalents of hydrogen. The sum is again equal to eight. The relation between Cl_2O_7 and ClH is the same. This shows that the property of elements of combining with such different elements as oxygen and hydrogen, is subject to one common rule, which is also formulated in the system of the elements presently to be described.[7]

In the preceding we see not only the regularity and simplicity

[7] The hydrogen compounds, R_2H, in equivalency correspond with the type of the suboxides, R_4O. Palladium, sodium and potassium give similar hydrogen compounds, and it is worthy of remark that according to the periodic system these elements stand near to each other, and that in those groups where the hydrogen compounds R_2H appear, the quaternary oxides R_4O are also present.

Not wishing to complicate the exposition, I here only touch on the general features of the relation between the hydrates and oxides and of the oxides among themselves.

which govern the formation and properties of the oxides and of all the compounds of the elements, but also a fresh and exact means for recognising the analogy of elements. Analogous elements give compounds of analogous types, both higher and lower. If CO_2 and SO_2 are two gases which closely resemble each other both in their physical and chemical properties, the reason of this must not be looked for in an analogy of sulphur and carbon ; but it lies in that identity of the type of combination, RX_4, in which both oxides appear, and in that influence which a large mass of oxygen always exerts on the properties of its compounds. In fact, there is little resemblance between carbon and sulphur, as is seen not only from the fact that CO_2 is the *higher form* of oxidation, whilst SO_2 is able to further oxidise into SO_3, but also from the fact that all the other compounds—for example, SH_2 and CH_4, SCl_2 and CCl_4, &c.—are entirely unlike both in type and in chemical properties. This absence of analogy in carbon and sulphur is clearly expressed in the fact that the higher oxides are of different composition, CO_2 for carbon, and SO_3 for sulphur. The halogens, which are analogous, give both like higher and lower compounds. So also do the metals of the alkaline earths and of the alkalis. Many such groups of analogous elements have long been known. Thus there are analogues of oxygen, nitrogen, and carbon, and we shall meet with many such groups. But an acquaintance with them involuntarily leads to the questions, what is the cause of analogy and what is the relation of one group to another? If these questions remain unanswered, it is easy to fall into error in the formation of the groups because the notions of the degree of analogy will always be relative, and will not present any accuracy or distinctness. Thus lithium is analogous in some respects to potassium and in others to magnesium ; or beryllium is analogous to both aluminium and magnesium. In thallium, as we shall afterwards see and as was observed on its discovery, there is much in kindred with lead and mercury, but some of its properties appertain to lithium and potassium. Naturally, where it is impossible to make measurements one is involuntarily obliged to limit oneself to approximation or comparison, founded on

Thus, for instance, the conception of the ortho-acids and of the normal acids will be considered in speaking of phosphoric and phosphorous acids.

As in the further exposition of the periodic law only those oxides which give salts will be considered, I think it will not be superfluous to here mention the following facts relative to the peroxides. Of the *peroxides* corresponding with hydrogen peroxide, the following are at present known: H_2O_2, Na_2O_2, S_2O_7 (as HSO_4?), K_2O_4, K_2O_2, CaO_2, TiO_3, Cr_2O_7, CuO_2(?), Rb_2O_2, SrO_2, Ag_2O_2, CsO_2, Cs_2O_2, BaO_2 and MO_4. It is probable that the number of peroxides will increase with further investigation. A periodicity is seen in those now known because the elements (excepting Li) of the first group, which gives R_2O, form peroxides, and then the elements of the fourth group seem also to be particularly inclined to form peroxides.

apparent signs which are not distinct and are void of exactitude. But in the elements there is one accurately measurable property, which is subject to no doubt—namely, that property which is expressed in their atomic weights. Its magnitude indicates the relative mass of the atom, or, if we avoid the conception of the atom, its magnitude shows the relation between the masses forming the chemical and independent individuals or elements. And according to the sense of all our physico-chemical data, the mass of a substance is that property on which all the remaining properties of matter must be dependent, because they are all determined by similar conditions or by those forces which act in the weight of a substance, and this is directly proportional to the mass of a substance. Therefore, it is most natural to seek for a dependence between the properties and analogies of the elements on the one hand and their atomic weights on the other.

This is the fundamental idea which leads *to arranging all the elements according to their atomic weights.* A repetition of properties is then immediately observed in the periods of the elements. We are already familiar with examples of this—

F =19,	Cl=35·5,	B =80,	I =127
Na=23,	K =39,	Rb=85,	Cs=133
Mg=24,	Cu=40,	Sr=87,	Ba=137.

The substance of the matter is seen in these groups. The halogens have smaller atomic weights than the alkali metals, and the latter than the metals of the alkaline earths. Therefore, *if all the elements be arranged in the order of their atomic weights a periodic repetition of properties is obtained.* This is expressed by the *law of periodicity; the properties of the elements, as well as the forms and properties of their compounds, are in periodic dependence or, expressing ourselves algebraically, form a periodic function of the atomic weights of the elements.*[8] Table I. of *the periodic system of the elements*, which

[8] The periodic law and the periodic system of the elements appeared in the same form as here given in the first edition of this work, begun in 1868 and finished in 1871. In laying out the accumulated information respecting the elements, I had occasion to reflect on their metrical relations. At the beginning of 1869 I distributed among many chemists a tract entitled, 'An Experimental System of the Elements, based on their Atomic Weights and Chemical Analogies,' and at the March meeting of the Russian Chemical Society, 1869, I communicated a paper 'On the Correlation of the Properties and Atomic Weights of the Elements.' The substance of this paper is embraced in the following conclusions: (1) The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties. (2) Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (platinum, iridium, osmium) or which increase regularly (*e.g.* potassium, rubidium, cæsium). (3) The arrangement of the elements or of groups of elements in the order of their atomic weights,

is placed at the very beginning of this book, is composed according to this law. It is arranged in conformity with the eight types of oxides described in the preceding pages, and those elements which give the oxides R_2O, and consequently salts RX, form the 1st group; the elements giving R_2O_2 or RO as their highest grade of oxidation enter into the 2nd group, those giving R_2O_3 as their higher oxides form the

corresponds with their so-called *valencies*. (4) The elements, which are the most widely diffused in nature, have *small* atomic weights, and all the elements of small atomic weight are characterised by their sharply-defined properties. They are therefore typical elements. (5) The *magnitude* of the atomic weight determines the character of an element. (6) The discovery of many yet unknown elements may be expected. For instance, elements analogous to aluminium and silicon, whose atomic weights would be between 65 and 75. (7) The atomic weight of an element may sometimes be amended by aid of a knowledge of those of the contiguous elements. Thus the combining weight of tellurium must lie between 123 and 126, and cannot be 128. (8) Certain characteristic properties of the elements can be foretold from their atomic weights.

The entire periodic law is included in these lines. In the series of subsequent papers (1870–72, for example, in the *Transactions* of the Russian Chemical Society, of the Moscow meeting of Naturalists of the Petroffsky Academy, and Liebig's *Annalen*) on the same subject, we only find applications of the same principles, which were afterwards confirmed by the labours of Roscoe, Carnelley, Thorpe, and others in England, of Rammelsberg (respecting cerium and uranium), L. Meyer (respecting the specific volumes of the elements), Zimmermann (respecting uranium), and more especially of C. Winkler (who discovered germanium, and showed its identity with ekasilicon), and others in Germany; of Lecoq de Boisbaudran in France (the discovery of gallium = ekaaluminium), of Cleve respecting the atomic weights of the cerium metals), Nillson (discoverer of scandium = ekaboron), and Nillson and Pettersson (determination of the vapour density of beryllium chloride) in Sweden, and of Brauner (who investigated cerium, and determined the combining weight of tellurium = 125), in Austria.

I consider it necessary to state, that in arranging the periodic system of the elements I made use of the previous researches of Dumas, Gladstone, Pettenkofer, Kremers, and Lenssen on the atomic weights of related elements, but I was not acquainted with the works preceding mine of De Chancourtois (*vis tellurique*, or the spiral of the elements according to their properties and equivalents) in France, and of J. Newlands (Law of Octaves—for instance, H, F, Cl, Co, Br, Pd, I, Pt form the first octave, and O, S, Fe, Se, Rh, Te, Au, Th the last) in England, although certain germs of the periodic law are to be seen in these works. With regard to the work of Prof. Lothar Meyer respecting the periodic law (Notes 12 and 13), it is evident, judging from the method of investigation, and of his statement (Liebig's *Annalen Supt. Band* 7, 1870, 354), at the very commencement of which he cites my paper of 1869 above mentioned, that he took the periodic law in the same form as it was given by me.

In conclusion to this historical statement I consider it well to observe that no law of nature, however general, has been established at once; its establishment is always preceded by many presentiments, but the acknowledgment of a law does not take place when it is recognised in all its significance, but only when it has been confirmed by experiment, which the scientific man must look to as the only proof of the correctness of his conjectures and opinions. I therefore, for my part, consider Roscoe, De Boisbaudran, Nillson, Winkler, Brauner, Carnelley, Thorpe, and others who verified the adaptability of the periodic law to chemical reality, as the true founders of the periodic law, the further development of which still awaits fresh workers. The efforts made in this direction, which are mentioned in the following notes, cannot for the present be considered as in any way elucidating many questions which involuntarily arise on an acquaintance with this law.

3rd group, and so on, whilst the elements of all the groups which are nearest in their atomic weights are arranged in series from 1 to 12. The even and uneven series of the same groups present the same forms, but differ in their properties, and therefore two contiguous series, one even and the other uneven—for instance, the 4th and 5th—form a period. Hence the elements of the 4th, 6th, 8th, 10th, and 12th, or of the 3rd, 5th, 7th, 9th, and 11th series form analogues, like the halogens, alkali metals, &c. The conjunction of two series, one even and its contiguous uneven series, thus forms one large *period*. These periods, beginning with the alkali metals, end with the halogens. The elements of the two first series have the least atomic weights, and in consequence of this very circumstance, although they bear the general properties of a group, still they show many peculiar and independent properties.[9] Thus fluorine, as we know, differs in many points from the other halogens, and lithium from the other alkali metals, and so on. These lightest elements may be termed *typical elements*. They include—

H.
Li, Be, B, C, N, O, F.
Na, Mg . . . . .

In the annexed table all the remaining elements are arranged, not in groups and series, but *according to periods*. In order to penetrate into the essence of the matter, it must be remembered that here the atomic weight gradually increases along a given line; for instance, in the line commencing with K=39 and ending with Br (the 17th)=80, the intermediate elements have intermediate atomic weights.

Even Series.																
											Mg	Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Cs	Ba	La	Ce	Di	?	—	—	—	—	—	—	—	—	—	—	—
—	—	Yb	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—
—	—	—	Th	—	U											
											Uneven Series.					

The same degree of analogy as we know to exist between potassium, rubidium, and cæsium; or chlorine, bromine, and iodine; or calcium, strontium, and barium also exists between the elements of the other vertical columns. Thus, for example, zinc, cadmium, and mercury,

[9] This resembles the fact, well known to those having an acquaintance with organic chemistry, that in a series of homologues (Chap. VIII.) the first members, in which there is the least carbon, although showing the general properties of the homologous series, still present certain distinct peculiarities.

which are described in the following chapter, present a very close analogy with magnesium. All our further descriptions of the elements will be arranged according to this periodic system. The distribution of the elements in groups, series, and periods is shown in the tables given in this chapter, at the end of the preface, and at the end of the book. For a true comprehension of the matter, it is very important to see at once, that all the given aspects [10] of the distribution

[10] Besides arranging the elements (*a*) in a successive order according to their atomic weights, with indication of their analogies by showing some or other properties (both chemical—for instance, their power of giving one or another form of combination—and physical), both of the *elements* and of their compounds (as is done in Table III. at the beginning of this volume), (*b*) according to periods (as is done in Table I. at the commencement of volume I. after the preface), and (*c*) according to groups and series or small periods (as is done in Table II. and in Table IV. at the end of this volume), I am acquainted with the following methods of expressing the periodic relations of the elements: (1) By a curve drawn through points obtained in the following manner: The elements are arranged along the horizontal axis of abscissæ at distances from zero proportional to their atomic weights and the values for each of the elements of some property—for example, specific volumes or melting points are expressed by the ordinates. This method, although graphic, has the theoretical disadvantage that it does not in any way indicate the existence of a limited and definite number of elements in each period. There is nothing, for instance, in this method of expressing the law of periodicity to show that between magnesium and aluminium there can be no other element with an atomic weight of say 25, atomic volume 13, and in general having properties intermediate between those of these two elements. The actual periodic law does not correspond with a continuous change of properties, with a continuous variation of atomic weight—in a word, it does not express an uninterrupted function—and as the law is purely chemical, starting from the conceptions of atoms and molecules which combine in multiple proportions, with intervals (not continuously), it, *above all*, depends on there being but few types of compounds, which are arithmetically simple, *repeat themselves*, and offer no uninterrupted transitions, and therefore each period can only contain a definite number of members. For this reason there can be no other elements between magnesium, which gives the chloride $MgCl_2$, and aluminium, which forms AlX_3; there is a break in the continuity, according to the law of multiple proportions. The periodic law ought not, therefore, to be expressed by geometrical figures in which continuity is always understood. Owing to these considerations I have never, and will never, express the periodic relations of the elements by any geometrical figures. (2) *By a plane spiral.* Radii are traced from a centre, proportional to the atomic weights; analogous elements lie along one radius, and the points of intersection are arranged in a spiral. This method, adopted by De Chancourtois, Baumgauer, E. Huth, and others, has many of the imperfections of the preceding, although it removes the indefiniteness as to the number of elements in a period. In it one ought only to see a simple endeavour to bring the complex relations under a simple graphic representation, because the number of radii and the formulation of the spiral is not dependent on any conditions. (3) *By the lines of atomicity*, either parallel, as in Reynolds's and the Rev. S. Haughton's method, or as in Crookes's method, inclined to the right and left of an axis, along which the magnitudes of the atomic weights are counted, the points of the elements are marked off, on the one side the members of the even series (paramagnetic, like oxygen, potassium, iron), and on the other side the members of the uneven series (diamagnetic, like sulphur, chlorine, zinc, and mercury). On joining up these points a periodic curve is obtained, likened by Crookes to the oscillations of a pendulum, and, according to Haughton, representing a cubical curve. This method would be very graphic did it not require, for instance, that sulphur should be considered as bivalent and manganese as univalent, although

of the elements according to their atomic weights essentially express one and the same fundamental *dependence—periodic properties.*[11] The following points must then be seen in it.

neither of these elements gives stable derivatives of these natures, and although the one is taken on the basis of the lowest possible compound SX_2, and the other of the highest, because manganese may be referred to the univalent elements only by the analogy of $KMnO_4$ to $KClO_4$. Furthermore, Reynolds and Crookes place hydrogen, iron, nickel, cobalt, and others outside the axis of atomicity, and consider uranium as bivalent without the least foundation. (4) Rantsheff endeavoured to classify the elements in their periodic relations by a system dependent on solid geometry. He communicated this mode of expression to the Russian Chemical Society, but his communication, which is apparently not void of interest, has not yet appeared in print. (5) *By algebraic formulæ*: for example, E. J. Mills (1886) endeavours to express all the atomic weights by the logarithmic function $A=15\ (n-0{\cdot}9375t)$, in which the variables n and t are whole numbers. For instance, for oxygen $n=2$, $t=1$, hence $A=15{\cdot}94$; for antimony $n=9$, $t=0$, whence $A=120$, and so on. n varies from 1 to 16 and t from 0 to 59. The analogues are hardly distinguishable by this method, thus for chlorine the magnitudes of n and t are 3 and 7, for bromine 6 and 6, for iodine 9 and 9, for potassium 3 and 14, for rubidium 6 and 18, for cæsium 9 and 20; but a certain regularity seems to be shown. (6) A more natural method of expressing the dependence of the properties of elements on their atomic weights is obtained by *trigonometrical functions*, because this dependence is periodic like the functions of trigonometrical lines, and therefore Ridberg in Sweden (1885) and F. Flavitzky in Russia (Kazan, 1887) have adopted a like method of expression, which must be considered as worthy of being worked out, although it does not express the absence of intermediate elements—for instance, between magnesium and aluminium, which is essentially the most important part of the matter. (7) The investigations of B. N. Tchitchérin (1888, *Journal of the Russian Physical and Chemical Society*) form the first effort in the latter direction. He carefully studied the alkali metals, and discovered the following simple relation between their atomic volumes: they can all be expressed by $A(2-0{\cdot}0428An)$, where A is the atomic weight and $n=1$ for lithium and sodium, $\frac{1}{2}$ for potassium, $\frac{3}{8}$ for rubidium, and $\frac{2}{5}$ for cæsium. If n always $= 1$, then the volume of the atom would become zero at $A=46\frac{2}{3}$, and would reach its maximum when $A=23\frac{1}{3}$, and the density increases with the growth of A. In order to explain the variation of n, and the relation of the atomic weights of the alkali metals to those of the other elements, as also the atomicity itself, Tchitchérin supposes all atoms to be built up of a primary matter; considers the relation of the central to the peripheric mass, and, guided by mechanical principles, deduces many of the properties of the atoms from the reaction of the internal and peripheric parts of each atom. This endeavour offers many interesting points, but the value of the theory cannot be judged at present, as it is not yet fully developed. Further, it admits the hypothesis of the building up of all the elements from one primary matter, and at the present time such an hypothesis has not the least support either in theory or in fact. Besides which the starting-point of the theory is the specific gravity of the metals at a definite temperature (it is not known how the above relation would appear at other temperatures), and the specific gravity varies even under mechanical influences.

[11] Many natural phenomena exhibit a dependence of a periodic character. Thus the phenomena of day and night and of the seasons of the year, and vibrations of all kinds, exhibit variations of a periodic character in dependence on time and space. But in ordinary periodic functions one variable varies continuously, whilst the other increases to a limit, then a period of decrease begins, and having in turn reached its limit, a period of increase again begins. It is otherwise in the periodic function of the elements. Here the mass of the elements does not increase continuously, but abruptly, by steps, as from magnesium to aluminium. So also the valency or atomicity leaps directly from 1 to 2 to 3, &c., without intermediate quantities, and in my opinion it is these properties which

1. The formulæ of the higher oxygen compounds are determined by the groups; the first group gives R_2O, the second R_2O_2 or RO, the third R_2O_3, &c. There are eight types of oxides and therefore eight

are the most important, and it is their periodicity which forms the substance of the periodic law. It expresses *the properties of the real elements*, and not of what may be termed their manifestations visually known to us. The external properties of elements and compounds are in periodic dependence on the atomic weight of the elements only because these external properties are themselves the result of the properties of the real elements forming the isolated elements or the compound. To explain and express the periodic law is to explain and express the cause of the law of multiple proportions, of the difference of the elements, and the variation of their atomicity, and at the same time to understand what mass and gravitation are. In my opinion this is now premature. But just as without knowing the cause of gravitation, it is possible to make use of the law of gravity, so for the aims of chemistry it is possible to take advantage of the laws discovered by chemistry without being able to explain their causes. The above-mentioned peculiarity of the laws of chemistry respecting definite compounds and the atomic weights leads one to think that the time has not yet come for their full explanation, and I do not think that it will come before the explanation of such primary laws of nature as the law of gravity.

It will not be out of place to here turn our attention to the many-sided correlation existing between the undecomposable *elements and the compound carbon radicles*, which has long been remarked (Pettenkofer, Dumas, and others), and reconsidered in recent times by Carnelley (1886), and most originally in Pelopidas's work (1883) on the principles of the periodic system. Pelopidas compares the series containing eight hydrocarbon radicles, C_nH_{2n+1}, C_nH_{2n}—for instance, C_6H_{13}, C_6H_{12}, C_6H_{11}, C_6H_{10}, C_6H_9, C_6H_8, C_6H_7, and C_6H_6—with the series of the elements arranged in eight groups. The analogy is particularly clear owing to the property of C_nH_{2n+1} to combine with X, thus reaching saturation, and of the following members with X_2, X_3 . . . X_8, and especially because these are followed by an aromatic radicle—for instance, C_6H_5—in which, as is well known, many of the properties of the saturated radicle C_6H_{13} are repeated, and in particular the power of forming a univalent radicle again appears. Pelopidas shows a confirmation of the parallel in the property of the above radicles of giving oxygen compounds corresponding with the groups in the periodic system. Thus the hydrocarbon radicles of the first group —for instance, C_6H_{13} or C_6H_5—give oxides of the form R_2O and hydroxides RHO, like the metals of the alkalis; and in the third group they form oxides R_2O_3 and hydrates RO_2H. For instance, in the series CH_3 the corresponding compounds of the third group will be the oxide $(CH)_2O_3$ or $C_2H_2O_3$—that is, formic anhydride and hydrate, CHO_2H, or formic acid. In the sixth group, with a composition of C_2, the oxide RO_3 will be C_2O_3, and hydrate $C_2H_2O_4$—that is, also a bibasic acid (oxalic) resembling sulphuric, among the inorganic acids. After carrying his views over a mass of organic compounds, Pelopidas lingers more particularly over the radicles corresponding with ammonium; for example, he takes methylammonium, $N(CH_3)H_3$ or NCH_6, in the first group, as showing many of the properties of the metals of the alkalis and giving an alkali, $NH_3(CH_3)(OH)$, like NaHO. In the second and following groups by the abstraction of hydrogen we obtain radicles all of higher atomicity and less alkaline character, and lastly in the seventh group we find CN, whose analogy to the halogens, corresponding with the seventh group, is well known.

With respect to this remarkable parallelism, it must above all be observed that in the elements the atomic weight increases in passing to contiguous members of a higher valency, whilst here it decreases, and therefore there is no foundation for seeing any indications in this correlation with the hydrocarbon radicles pointing towards a compound nature for the elementary substances; but rather that the periodic variability of elements and compounds is subject to some higher law whose nature, and still more whose cause, cannot at present be determined. It is probably based on the fundamental principles of the internal mechanics of the atoms and molecules, and as the periodic law has only been

groups. Two groups give a period, and the same type of oxide is met with twice in a period. For example, in the period beginning with potassium, oxides of the composition RO are formed by calcium and zinc, and of the composition RO_3 by molybdenum and tellurium. The oxides of the even series, of the same type, have stronger basic properties than the oxides of the uneven series, and the latter as a rule are endowed with an acid character. Therefore, the elements which exclusively give bases, like the alkali metals, will be at the commencement of the period, whilst such purely acid elements as the halogens will be at the end of the period. The interval will be occupied by intermediate elements, whose character and properties we shall afterwards describe. It must be observed that the acid character is chiefly proper to the elements with small atomic weights in the uneven series, whilst the basic character is exhibited by the heavier elements in the even series. Hence elements which give acids chiefly predominate among the lightest (typical) elements, especially in the last groups; whilst the heaviest elements, even in the last groups (for instance, thallium, uranium), have a basic character. Thus the basic and acid characters of the higher oxides are determined (*a*) by the type of oxide, (*b*) by the even or uneven series, and (*c*) by the atomic weight.

2. *The hydrogen compounds* being volatile or gaseous substances which are prone to reaction—such as HCl, H_2O, H_3N, and H_4C—are only formed by the elements of the uneven series and higher groups giving oxides of the forms R_2O_7, RO_3, R_2O_5, and RO_2.

3. If an element gives a hydrogen compound, RX_m, then it forms an *organo-metallic compound* of the same composition, where $X=C_nH_{2n+1}$: that is, X is the radicle of a saturated hydrocarbon. The elements of the uneven series, which are incapable of giving hydrogen compounds and which form oxides of the forms RX, RX_2, RX_3, also give organo-metallic compounds of this form proper to the higher oxides. Thus zinc forms the oxide ZnO, salts ZnX_2, and zinc-ethyl $Zn(C_2H_5)_2$. The elements of the even series do not seem to form organo-metallic compounds at all; at least all efforts for their preparation have as yet been fruitless—for instance, in the case of titanium, zirconium, or iron.

4. The atomic weights of elements belonging to contiguous periods differ approximately by 45; for example, $K<Rb$, $Cr<Mo$, $Br<I$. But the elements of the typical series have the smallest atomic weight. The difference between the atomic weights of Li, Na, and $K=16$,

generally recognised for a few years it is not surprising that any further progress towards its explanation can only be looked for in the development of facts touching on this subject.

between Ca, Mg, and Br also 16, and between Si and C is 16, between S and O 16, and between Cl and F 16. As a rule, there is a greater difference between the atomic weights of the elements of one group and those of its two neighbouring series (Ti—Si=V—P=Cr—S=Mn—Cl=Nb—As, &c.=20), and this difference attains a maximum with the heaviest elements (for example, Th—Pb=26, Bi—Ta=26, Ba—Cd=25, &c.). Furthermore, the difference between the atomic weights of the elements of even and uneven series also increases. In fact, the differences between Na and K, Mg and Ca, Si and Ti are less abrupt than those between Pb and Th, Ta and Bi, Cd and Ba, &c. Thus there is even in the magnitude of the differences of the atomic weights of analogous elements a certain connection observable with the gradation of their properties.[12]

5. Every element, according to the periodic system, occupies a certain position, determined by the group (indicated in Roman numerals) and series (Arabic numerals) in which it occurs. They indicate the atomic weight, the analogues, properties, and type of the higher oxide, and of the hydrogen and other compounds—in a word, all the chief quantitative and qualitative features of an element, although there yet further remain a whole series of details and peculiarities, whose cause, according to the sense of the whole doctrine lying at the base of the system, must be looked for in small differences of the atomic weights. If in a certain group there occur elements, R_1, R_2, R_3, and if in that series which contains one of these elements, for instance R_2, an element Q_2 precedes it and an element T_2 succeeds it. Then, the properties of R_2 are determined by the properties of R_1, R_3, Q_2, and T_2. Thus, for instance, the atomic weight of $R_2=\frac{1}{4}(R_1+R_3+Q_2+T_2)$.

[12] The relation between the atomic weights, and especially the difference = 16, was observed in the sixth and seventh decades of this century by Dumas, Pettenkofer, L. Meyer, and others. Thus Lothar Meyer in 1864, following Dumas and others, grouped together the tetravalent elements carbon and silicon; the trivalent elements nitrogen, phosphorus, arsenic, antimony, and bismuth; the bivalent oxygen, sulphur, selenium, and tellurium; the univalent fluorine, chlorine, bromine, and iodine; and the univalent metals lithium, sodium, potassium, rubidium, cæsium, and thallium, and the bivalent metals beryllium, magnesium, strontium, and barium—observing that in the first the difference is, in general = 16, in the second about = 46, and the last about = 87–90. The first germs of the periodic law are visible in such observations as these. Since its establishment this subject has been most fully worked out by Ridberg (Note 10), who observed a periodicity in the variation of the differences between the atomic weights of two contiguous elements, and its relation to their atomicity. A. Bazaroff (1887) investigated the same subject, taking, not the arithmetical differences of contiguous and analogous elements, but the ratio of their atomic weights, and he also observed that this ratio alternately rises and falls with the rise of the atomic weights.

I will here remark that the relation of the eighth group to the others will be considered at the end of this work (it includes iron, cobalt, nickel, copper, and their analogues).

For example, selenium occurs in the same group as sulphur, S=32, and tellurium, Te=125, and in the 7th series, As=75 stands before it and Br=80 after it. Hence the atomic weight of selenium should be $\frac{1}{2}(32+125+75+80)=78$, as it is in reality. Other properties of selenium may also be determined in this manner. For example, arsenic forms H_3As, bromine gives HBr, and it is evident that selenium, which stands between them, should form H_2Se, with properties intermediate between those of H_3As and HBr. Even the physical properties of selenium and its compounds, not to speak of their composition, determined by the group in which it occurs, may be foreseen with a close approach to reality from the properties of sulphur, tellurium, arsenic, and bromine. *In this manner it is possible to foretell the properties of still unknown elements.* For instance, in the position IV, 5—that is, in the IVth group and 5th series—an element is still wanting. These unknown elements may be named after the preceding known element of the same group, by adding to the first syllable the prefix *eka*, which means *one* in Sanskrit. The element IV, 5, follows after IV, 3, and this position is occupied by silicon, and therefore we call the unknown element ekasilicon and its symbol, Es. The following are the properties which this element should have on the basis of the known properties of silicon, tin, zinc, and arsenic. Its atomic weight is nearly 72, higher oxide EsO_2, lower oxide EsO, compounds of the general form EsX_4, and chemically unstable lower compounds of the form EsX_2. Es gives volatile organo-metallic compounds—for instance, $Es(CH_3)_4$, $Es(CH_3)_3Cl$, and $Es(C_2H_5)_4$, which boil at about 160°, &c., also a volatile and liquid chloride, $EsCl_4$, boiling at about 90° and of sp. gr. about 1·9. EsO_2 will be the anhydride of a feeble colloidal acid, metallic Es will be rather easily obtainable from the oxides and from K_2EsF_6 by reduction, EsS_2 will resemble SnS_2 and SiS_2, and will probably be soluble in ammonium sulphide; the sp. gr. of Es will be about 5·5, EsO_2 will have a density of about 4·7, &c. Such a prediction of the properties of ekasilicon was made by me in 1871; and now that this element has been discovered by C. Winkler of Freiberg it has been found that its actual properties entirely correspond with those which were foretold.[13] In this we see a most important

[13] The laws of nature admit of no exceptions, and in this they clearly differ from such rules and maxims as are found in grammar, &c. The confirmation of a law is only possible by means of the deduction of the consequences proceeding from it, and which would without it be impossible and unforeseen, and by verifying these consequences by experiment and further proofs. Therefore, when I saw the periodic law, I (1869–1871, Note 9) deduced such logical consequences from it as could show whether it were true or not. Among them was the prediction of the properties of undiscovered elements and the correction of the atomic weights of many, and at that time little known, elements.

confirmation of the truth of the periodic law. This element is now called germanium, Ge. It is not the only one that has been foretold by the periodic law.[14] We shall see in describing the elements of the third group, that properties were foretold of an element ekaaluminium, III, 5, El=68, and were afterwards verified when the metal termed 'gallium' was discovered. So also the properties of scandium corresponded with those predicted for ekaboron.[15]

Thus uranium, for example, was considered as trivalent, U=120; but as such it did not correspond with the periodic law. I therefore proposed to double its atomic weight—U=240, and the researches of Roscoe, Zimmermann, and others justified this alteration. It was the same with cerium, whose atomic weight it was necessary to change according to the periodic law. I therefore determined its specific heat, and the result I obtained was verified by the new determinations of Hillebrand. I then corrected certain formulæ of the cerium compounds, and the researches of Rammelsberg, Brauner, Cleve, and others verified the proposed alteration. It was necessary to do one or the other—either to consider the periodic law as completely true, and as forming a new instrument in chemical research, or to refute it. Acknowledging the method of experiment to be the only true one, I myself verified what I could, and gave every one the possibility of proving or confirming the law, and did not think, like L. Meyer (Liebig's *Annalen, Supt. Band* 7, 1870, 364), when writing about the periodic law, that 'it would be rash to change the accepted atomic weights on the basis of so uncertain a starting-point.' ('Es würde voreilig sein, auf so unsichere Anhaltspunkte in eine Aenderung der bisher angenommenen Atomgewichte vorzunehmen.') In my opinion, the basis offered by the periodic law had to be verified or refuted, and experiment in every case verified it. The starting-point then became general. No law of nature can be established without such a method of testing it. Neither De Chancourtois, to whom the French ascribe the discovery of the periodic law, nor Newlands, who is put forward by the English, nor L. Meyer, who is now cited by many as its founder, ventured to foretell the *properties* of undiscovered elements, or to alter the 'accepted atomic weights,' or, in general, to regard the periodic law as a new, strictly-established law of nature, as I did from the very beginning (1869), and therefore the *regularities* observed by them, which moreover were then unknown to me, can only be considered as a preparative to the discovery of the law. So the way was prepared for the laws of spectroscopy before Kirchhoff, for the mechanical theory of heat before Meyer, Joule, and Clausius, and even for the discoveries essentially belonging to Lavoisier and Newton before they took the matter in hand. In clothing my modest labours with such great names and examples I only wish to protect myself from those reproaches to which I should be subject did I not touch on the history of the birth of the periodic law, for much has been written about it since the properties of gallium, scandium, and germanium established this law as a new truth, permitting the invisible to be seen and the unknown known.

[14] When, in 1871, I wrote a paper on the application of the periodic law to the determination of the properties of yet undiscovered elements, I did not think I should live to see the verification of this consequence of the law, but such was to be the case. Three elements were described—ekaboron, ekaaluminium, and ekasilicon—and now, after the lapse of twenty years, I have had the great pleasure of seeing them discovered and named after those three countries where the rare minerals containing them are found, and where they were discovered—Gallia, Scandinavia, and Germany.

[15] Taking indium, which occurs together with zinc, as our example, we will show the substance of the method employed. The equivalent of indium to hydrogen in its oxide is 37·7—that is, if we suppose its composition to be like that of water; then In=37·7, and the oxide of indium is In_2O. The atomic weight of indium was taken as double the equivalent—that is, indium was considered to be a bivalent element—and In=2×37·7=75·4. If indium only formed an oxide, RO, it should be placed in the II. group. But in this

6. As a true law of nature is one to which there are no exceptions, therefore the periodic dependence of the properties and the atomic weights of the elements gives a *new means for determining the atomic weight* or valency when the equivalent of an element is known. To several elements atomic weights had been given without any very accurate foundation, and to these no other means could as yet be applied for determining the true atomic weight. At the time (1869) when the periodic law was first proposed there were not a few such elements. It became possible to learn their true atomic weights, which were verified by later researches. Among the elements thus concerned were indium, uranium, cerium, yttrium, and others.

7. The periodic variability of the properties of the elements in dependence on their masses presents a distinction from other aspects of periodic dependences (as, for example, the sines of angles vary periodically and successively with the growth of the angles, or the temperature of the atmosphere with the course of time by yearly and daily periods), in that the masses of the atoms do not increase uninterruptedly, but by bounds; that is, according to the law of multiple proportions (Dalton's), there not only are not but there cannot be any transitive or intermediate elements between two

case it appears that there would be no place for indium in the system of the elements, because the positions II., 5 = Zn = 65 and II., 6 = Sr = 87 were already occupied by known elements, and according to the periodic law an element with an atomic weight 75 could not be bivalent. As neither the vapour density nor the specific heat, nor even the isomorphism (the salts of indium crystallise with great difficulty) of the compounds of indium were known, there was no reason for considering it to be a bivalent metal, and therefore it might be looked on as trivalent, quadrivalent, &c. If it be trivalent, then $In = 3 \times 37{\cdot}5 = 113$, and the composition of the oxide In_2O_3, and of its salts InX_3. In this case it at once falls into its place in the system, namely, in the III. group and 7th series, between Cl = 112 and Sn = 118, as an analogue of aluminium or dvialuminium (dvi = 2 in Sanskrit). All the properties observed in indium correspond with this position; for example, the density, cadmium = 8·6, indium = 7·4, tin = 7·2; the basic properties of the oxides CdO, In_2O_3, SnO_2, successively vary, so that the properties of In_2O_3 are intermediate between those of CdO and SnO_2 or Cd_2O_2 and Sn_2O_4. The fact of indium belonging to the III. group has been confirmed by the determination of its specific heat, and also by the fact that indium forms alums like aluminium, and therefore belongs to the same group.

The same kind of considerations necessitated taking the atomic weight of titanium as nearly 48, and not as 52, the figure derived from many analyses, and of Te = 125, and not 128. And both these corrections, made on the basis of the law, have now been confirmed, for Thorpe and Brauner respectively, by a series of careful experiments, found the atomic weights of titanium and tellurium to be those foreseen by the periodic law. Notwithstanding that previous analyses gave Os = 199·7, Ir = 198, and Pt = 187, the periodic law shows, as I remarked in 1871, that the atomic weights should rise from osmium to platinum and gold, and not fall. Many recent researches, and especially those of Seubert, have fully verified this statement, based on the law. Thus a true law of nature anticipates facts, foretells magnitudes, gives a hold on nature, and leads to improvements in the methods of research, &c.

neighbouring ones (for example, K=39 and Ca=40, or Al=27 and Si =28, or C=12 and N=14, &c.). As in a molecule of a hydrogen compound there may be either one, as in HF, or two, as in H_2O, or three, as in NH_3, &c., atoms of hydrogen, but as there cannot be molecules containing $2\frac{1}{2}$ atoms of hydrogen to one atom of an element, so there cannot be any element intermediate between N and O, with an atomic weight greater than 14 or less than 16. The nature of the periodic function of the elements is restricted by the fact that no atom retains more than 4 atoms of hydrogen, and no two atoms of an element more than 8 atoms of oxygen. This determines the eight groups of the elements.

8. The essence of the notions giving rise to the periodic law consists in a general physico-mechanical principle which recognises the correlation, transmutability, and equivalence of the forces of nature. Gravitation, attraction at small distances, and many other phenomena, are in direct dependence on the mass of matter. One cannot, therefore, but think that chemical forces also depend on mass. A dependence is shown, because the properties of elements and compounds are determined by the masses of the atoms of which they are formed. The weight of a molecule, or its mass, determines, as we have seen, many of its properties independently of its composition. Thus carbonic oxide, CO, and nitrogen, N_2, are two gases having the same molecular weight, and many of their properties (density, liquefaction, specific heat, &c.) are similar or nearly similar. The differences dependent on the nature of a substance play a secondary part, and form magnitudes of another order. So also the properties of atoms are mainly determined by their mass or weight. Only in this case there is a peculiarity in the dependence of the properties on the mass, for this *dependence is determined by a periodic law.* As the mass increases the properties at first successively and regularly vary, and then return to their original magnitude and recommence a fresh period of variation like the first. Nevertheless, here as in other cases a small variation of the mass of the atom generally leads to a small variation of properties, and determines differences of a second order. The atomic weights of cobalt and nickel, of rhodium, ruthenium, and palladium, and of osmium, iridium, and platinum, are very close to each other and their properties are also very much alike—the differences are not very perceptible. And if the properties of atoms form a function of their weight, then many notions which have more or less rooted themselves in chemistry must suffer change and be developed and worked out in the sense of this deduction, because the common idea of the chemical elements regards their atoms as independent and

individual, and considers that they evince their independent influence as determined by the *nature* of the atoms. Instead of this idea of the nature of the elements, one of *their mass* must now be established, and consequently it is necessary to consider, not the influence of an element taken individually, but to compare its influence on the one hand with that of the elements which, in their masses, stand close to it, and on the other hand with the elements belonging to the same group but to a different period. Many chemical deductions then acquire a new sense and significance, and a regularity is observed where it would otherwise escape attention. This is seen particularly clearly in the physical properties, to the consideration of which we shall afterwards turn, and we will now point out that first Gustavson (Chap. X. Note 28[b]) and then Potilitzin (Chap. XI. Note 66) demonstrated the direct dependence of the reactive power on the atomic weight and that fundamental property which is expressed in the forms of their compounds, whilst in a number of other cases the purely chemical relations of elements proved to be in connection with their periodic properties. As an instance in question, it may be mentioned that Carnelley remarked a dependence of the decomposability of the hydrates on the position of the elements in the periodic system, whilst L. Meyer, Willgerodt, and others established a connection between the atomic weight or the position of the metals in the periodic system, and their property of serving as mediums in the transference of the halogens to the hydrocarbons.[16] Keeping our attention in the same direction, determined by the periodic law, we see that the most widely distributed elements in nature are those with small atomic weights, whilst in organisms the lightest elements exclusively predominate (hydrogen, carbon, nitrogen, oxygen), whose small mass facilitates those transformations which are proper to organisms. Poluta (of Kharkoff), C. C. Botkin, Blake, and others even discovered a correlation between the physiological action of salts and other reagents on organisms, and

[16] Meyer, Willgerodt, and others, guided by the fact that Gustavson and Friedel had remarked that metalepsis rapidly proceeds in the presence of aluminium, investigated the action of nearly all the elements in this respect. For example, they took benzene, added the metals to be experimented on to it, and passed chlorine through the liquid in diffused light. When, for instance, sodium, potassium, barium, &c., are taken, there is no action on the benzene—that is, hydrochloric acid is not disengaged; but if aluminium, gold, or, in general, any metal having this power of aiding chlorination (Halogen-überträger), is employed, then the action is clearly seen from the volumes of hydrochloric acid evolved (especially if the metallic chloride formed is soluble in benzene). Thus, in the I. group, and in general among the even and light elements, there are none capable of serving as agents of metalepsis; but aluminium, gallium, indium, antimony, tellurium, and iodine, which are contiguous members in the periodic system, are excellent transmitters (carriers) of the halogens.

the positions occupied in the periodic system by the metals contained by them.[17]

As, from the essence of the matter, the physical properties must be in dependence on the composition of a substance and the nature of the elements forming it, so for them also one must expect a dependence on the atomic weight of the component elements, and consequently also on their periodic distribution. We shall meet with repeated proofs of this in the further exposition of our treatise, and for the present will content ourselves with citing the discovery by Carnelley in 1879 of the dependence of the magnetic properties of the elements on the position occupied by them in the periodic system. Carnelley showed that all the elements of the *even series* (beginning with lithium, potassium, rubidium, cæsium) belong to the number of magnetic (paramagnetic) substances; for example, according to Faraday and others, C, N, O, K, Ti, Cr, Mn, Fe, Co, Ni, Rh, Pd, Ce, Os, Ir, Pt are magnetic. And the elements of the *uneven series are diamagnetic*, H, Na, Si, P, S, Cl, Cu, Zn, As, Se, Br, Ag, Cd, Sn, Sb, I, Au, Hg, Tl, Pb, Bi.

Then Carnelley showed that the *melting-point* of elements varies periodically, as is seen by Table III., where all the most trustworthy data are collected, and those which are of the highest and least significance are clearly seen.[18] A like dependence is found on com-

[17] The periodic relations enumerated above appertain to the real elements, and not to the elements in the isolated state as we know them; and it is very important to note this, because the periodic law refers to the real elements, inasmuch as the atomic weight is proper to the real element and not to the isolated element, to which, as to a compound, a molecular weight is proper. Physical properties are chiefly determined by the properties of molecules, and only indirectly depend on the properties of the atoms forming the molecules. For this reason the periods, which are clearly and quite distinctly expressed—for instance, in the forms of combination—become to some extent involved (complicated) in the physical properties of their members. Thus, for instance, besides the *maxima* and *minima* corresponding with the periods and groups, new molecules appear; thus, as regards the melting-point of germanium, a local maximum appears, which was, however, foreseen by the periodic law when the properties of germanium (ekasilicon) were forecast.

[18] It is evident that many of the figures, especially those exceeding 1000°, have been determined with but little exactitude, and some (between brackets) are given by me only on the basis of rough and comparative determinations, which I have calculated from the melting-points of silver and platinum, now established by many observers. Besides the large periods whose maxima correspond with carbon, silicon, titanium, ruthenium (?), and osmium (?), there are also small periods in the melting-points, and their maxima correspond with sulphur, arsenic, antimony. The minima correspond with the halogens and metals of the alkalis. In the column following the melting-points are given the coefficients of linear expansion (chiefly according to Fizeau) in order to direct attention to the connection between these magnitudes and the melting-points. Raoul Pictet expressed this connection by the fact that he found the product $\alpha(t+273)\sqrt[3]{A/d}$ to be nearly constant for all elements in the free state, and nearly equal to 0·045, and being the coefficient of linear expansion, $t+273$, the melting-point calculated from the absolute zero (−273°), and $\sqrt[3]{A/d}$, the mean distance between the atoms, if A is the atomic weight and

paring the melting-points of the metallic chlorides, many of which were re-investigated for this purpose by Carnelley.[19]

d the sp. gr. of an element. Although the above product is not strictly constant (for example, for tin it is less than 0·03), nevertheless Pictet's rule gives an idea of the bond between magnitudes which ought to have a certain connection with each other.

[19] The melting-points (and boiling-points, in brackets) of the following chlorides are known, and a certain regularity is seen to exist in them, although the number of data is insufficient for its generalisation—

LiCl 598°	$BeCl_2$ 600°	BCl_3 −20°
NaCl 772°	$MgCl_2$ 708°	$AlCl_3$ 187°
KCl 734°	$CaCl_2$ 719°	$ScCl_3$?
CuCl 434° (993°)	$ZnCl_2$ 262° (680°)	$GaCl_3$ 76° (217°)
AgCl 451°	$CdCl_2$ 541°	$InCl_3$?
TlCl 427° (713°)	$PbCl_2$ 498° (908°)	$BiCl_3$ 227°

We will also enumerate the following data, which are not void of interest for comparison: HCl (−112°) (−102°); RbCl 710°, $SrCl_2$ 825°, CsCl 631°, $BaCl_2$ 860°, $SbCl_3$ 73° (223°), $TeCl_2$ 209° (327°), ICl 27°, $HgCl_2$ 276° (303°), $FeCl_3$ 306°, $NbCl_5$ 194° (240°), $TaCl_5$ 211° (242°), WCl_6 190°. The melting-points of the bromides and iodides are higher or lower than those of the corresponding chlorides, according to the atomic weight of the element and number of atoms of the halogen, as is seen from the following examples:—1. KCl 734°, KBr 699°, KI 634; 2. AgCl 454°, AgBr 427°, AgI 527°; 3. $PbCl_2$ 498° (900°), $PbBr_2$ 499° (861°), PbI_2 383° (906°); 4. $SnCl_4$ below −20° (114°), $SnBr_2$ 30° (201°), SnI_4 146° (295°).

Laurie (1882) also observed a periodicity in the *amount of heat* developed in the formation of the chlorides, bromides, and iodides (fig. 79), as it is seen from the following:

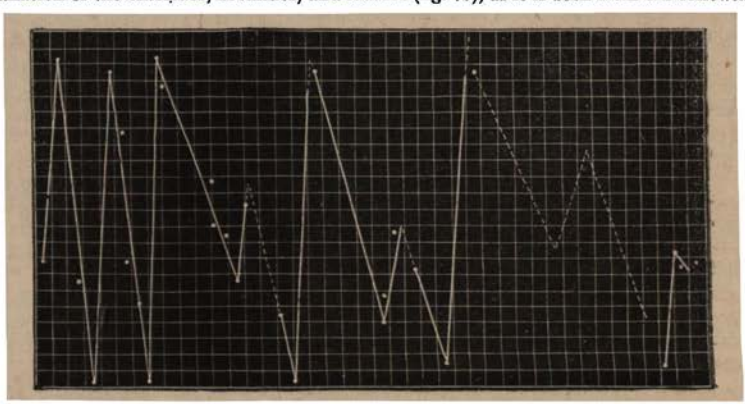

FIG. 79.—Laurie's diagram for expressing the periodic variation of the heat of formation of the chlorides. The atomic weights from 0 to 210 are laid along the abscissæ, and the amounts of heat from 0 to 220 thousand calories evolved in the combination with Cl_2 (*i.e.* with 71 parts of chlorine) are laid along the ordinates. The apexes of the curve correspond to Li, Na, K, Rb, Cs, and the lower extremities with F, Cl, Br, and I.

figures, where the heat developed is expressed in thousands of calories, and referred to a molecule of chlorine, Cl_2, so that the heat of formation of KCl is doubled, and that of $SnCl_4$ halved, &c.: Na 195 (Ag 59, Au 12), Mg 151 (Zn 97, Cd 93, Hg 63), Al 117, Si 79 (Sn 64), K 211 (Li 187), Ca 170 (Sr 185, Ba 194), whence it is seen that the greatest

There is no doubt that many other physical properties will, when further studied, also prove to be in periodic dependence on the atomic weights, but at present only a few are known with any completeness, and we will linger over the one which is the most easily and frequently determined—namely, the *specific gravity* in a solid and liquid state, the more especially as its connection with the chemical properties and relations of substances is shown at every step. Thus, for instance, of all the metals those of the alkalis, and of all the non-metals the halogens, are the most energetic in their reactions, and they have the least specific gravity among the adjacent elements, as is seen in Table III. Such are sodium, potassium, rubidium, cæsium among the metals, and chlorine, bromine, and iodine among the non-metals; and as such unenergetic metals as iridium, platinum, and gold (and even charcoal or the diamond) have the highest specific gravity among the elements near to them in atomic weight, therefore the degree of the condensation of matter evidently influences the course of the transformations proper to a substance, and furthermore this dependence on the atomic weight is of a clearly periodic character. In order to account for this to some extent, one may imagine that the lightest elements are porous, and, like a sponge, are easily penetrated by other substances, whilst the heavier elements are more compressed, and give way with difficulty to the insertion of other elements. These relations are best understood when instead of the specific gravities referring to a unit of volume,[20] the *atomic volumes of the elements*—that is, the quotient A/d of

amount of heat is evolved by the metals of the alkalis, and that in each period it falls from them to the halogens, which evolve very little heat in combining together.

In this respect it may not be superfluous to remark (1) that Thomsen, whose results I have employed above, already saw a correlation in the calorific equivalents of analogous elements, although he did not remark their periodic variation; (2) that the uniformity of many thermochemical deductions must gain considerably by the application of the periodic law, which evidently repeats itself in calorimetric data, and if these data frequently lead to true forecasts, this is due to the periodicity of the thermal, as well as of many other properties, as Laurie remarked; and (3) that the heat of formation of the oxides is also subject to a periodic dependence which differs from that of the heat of formation of the chlorides, in that the greatest quantity corresponds with the bivalent metals of the alkaline earths (magnesium, calcium, strontium, barium), and not with the univalent metals of the alkalis, as is the case with chlorine, bromine, and iodine. This circumstance is probably connected with the fact that chlorine, bromine, and iodine are univalent elements, and oxygen bivalent.

[20] Having occupied myself since the fifties (my dissertation for the degree of M.A. concerned the specific volumes, and is partially printed in the *Russian Mining Journal* for 1856) with the problems concerning the relations between the specific gravities and volumes, and the chemical compositions of substances, I am inclined to think that the direct investigation of specific gravities gives essentially the same results as the investigation of specific volumes, only that the latter are more graphic. Table III. of the periodic properties of the elements clearly illustrates this. Thus, for those members whose volume is the greatest among the contiguous elements, the specific gravity is least.

the atomic weight A by the specific gravity d—are taken for comparison. As, according to the whole sense of the atomic doctrine, the actual matter of a substance does not fill up its whole cubical contents, but is surrounded by a medium (ethereal, as is often imagined), like the stars and planets which travel in the space of the heavens and fill it, with greater or less intervals, so the quotient A/d only expresses the *mean* volume corresponding to the sphere of the atoms, and therefore $\sqrt[3]{A/d}$ is *the mean distance between the centres of the atoms.* For compounds whose molecules weigh M, the mean magnitude of the atomic volume is obtained by dividing the mean molecular volume M/d by the number of atoms n in the molecule.[21] The above relations may easily be expressed in this sense by comparing the atomic volumes. Those comparatively light elements which easily and frequently enter into reaction have the greatest atomic volumes: sodium 23, potassium 45, rubidium 57, cæsium 71, and the halogens about 27; whilst with those elements which enter into reaction with difficulty, the mean atomic volume is small; for carbon in the form of the diamond it is less than 4, as charcoal about 6, nickel and cobalt less than 7, iridium and platinum about 9. The remaining elements having atomic weights and properties intermediate between those elements mentioned above have also intermediate atomic volumes. Therefore *the specific gravities and specific volumes of solids and liquids*, like all their other properties, *stand in periodic dependence on the atomic weights*, as is seen in Table III., where both A (the atomic weight) and d (the specific gravity), and A/d (specific volumes of the atoms) are given.

Thus we find that in the periods beginning with lithium, sodium, potassium, rubidium, cæsium, and ending with fluorine, chlorine, bromine, iodine, the extreme members (energetic elements) have a small density and large volume, whilst the intermediate substances gradually increase in density and decrease in volume—that is, as the

—that is, the periodic variation of both properties is equally evident. In passing, for instance, from silver to iodine we have a successive decrease of sp. gr. and successive increase of sp. volume. The periodic alternation of the rise and fall of the sp. gr. and sp. vol. of the free elements was communicated by me in August 1869 to the Moscow Meeting of Russian Naturalists. In the following year, 1870, L. Meyer's paper, also respecting the sp. vol. of the elements, appeared.

[21] In my opinion the mean volume of the atoms of compounds deserves more attention than has yet been paid to it. I may point out, for instance, that for feebly energetic oxides the mean volume of the atom is generally nearly 7; for example, the oxides SiO_2, Sc_2O_5, TiO_2, V_2O_5, as well as ZnO, Ga_2O_3, GeO_2, ZrO_2, In_2O_3, SnO_2, Sb_2O_5, &c., whilst the mean volume of the atom of the alkali and acid oxides is greater than 7. Thus we find in the magnitudes of the mean volumes of the atom in oxides and salts both a periodic variation and a connection with their energy of essentially the same character as occurs in the case of the free elements.

atomic weight increases the density rises and falls, again rises and falls, and so on. Furthermore, the energy decreases as the density rises, and the greatest density is proper to the atomically heaviest and least energetic elements.

In order to explain the relation between the volumes of the elements and of their compounds, Table III. gives the densities and volumes of the higher saline oxides of the majority of the elements arranged in the same order as in the case of the elements. For convenience of comparison the volumes of the oxides are all calculated per two atoms of an element combined with oxygen. For example, the density of $Al_2O_3=4{\cdot}0$, weight $Al_2O_3=102$, volume $Al_2O_3=25{\cdot}5$. Whence it is directly seen that, knowing the volume of aluminium to be 11 in the formation of aluminium oxide, 22 of its volumes give 25·5 volumes of oxide.

Above all a distinct periodicity may also be observed with respect to the specific gravities and volumes of the higher saline oxides. So in each period, beginning with the alkali oxides, the specific gravity first rises, reaches a maximum, and then falls on passing to the acid oxides, and again becomes a minimum about the halogens. But it is especially important to turn attention to the fact that the volume of the alkali oxides is less than that of the metal contained in them, which is also expressed in the tenth column, giving this difference per one atom of oxygen.[22] Thus 2 atoms of sodium, or 46 volumes, give 24 volumes of Na_2O, and about 37 volumes of 2NaHO—that is, the oxygen and hydrogen in distributing themselves in the medium of sodium, have not only not increased the distance between its atoms, but have brought them nearer together, have drawn them together by the force of their great affinity, and evidently by reason of the small mutual attraction of the atoms of sodium. Such metals as aluminium and zinc, in combining with oxygen and forming oxides of feeble salt-forming capacity, hardly vary in volume, but the common metals and non-metals, and especially those forming acid oxides, always give an increased volume when oxidised—that is, the atoms are set further apart in order to make room for the oxygen. The oxygen in them does not compress

[22] The volume of oxygen (Table III. column 10) is evidently a variable quantity, forming a distinctly periodic function of the atomic weight and type of the oxide, and therefore the efforts which were formerly made to find the volume of the atom of oxygen in the volumes of its compounds may be considered to be futile. But as a distinct contraction takes place in the formation of oxides, if the volume of an oxide is frequently less than the volume in the free state of the element contained in it, one would think that the volume of oxygen in a free state is between 12 and 15, judging from the figures given in the second column, and therefore the specific gravity (Vol. I. p. 162) of solid oxygen in a free state would be about 0·9.

the molecule as in the alkalis; it is therefore comparatively easily disengaged.

As the volumes of the chlorides, organo-metallic and all other corresponding compounds also vary in a like periodic succession with a change of elements, it is evidently possible to indicate the properties of substances yet uninvestigated by experimental means, and even those of yet undiscovered elements. It was possible by following this method to foretell, on the basis of the periodic law, many of the properties of scandium, gallium, and germanium, which were verified with great accuracy after these metals had been discovered.[23] Therefore, the periodic law has not only embraced the mutual relations of the elements and expressed their analogy, but has also to a certain extent subjected to law the doctrine of the types of the compounds formed by the elements; has enabled us to see a regularity in the variation of all chemical and physical properties of elements and compounds, and has rendered it possible to foretell the properties of elements and compounds yet uninvestigated by experimental means; it therefore prepares the ground for the building up of atomic and molecular mechanics.[24]

[23] As an example we will take indium oxide, In_2O_3. Its sp. gr. and sp. vol. should be the mean of those of cadmium oxide, Cd_2O_2, and stannic oxide, Sn_2O_4, as indium stands between cadmium and tin. Thus in the seventies it was already evident that the volume of indium oxide should be about 38, and its sp. gr. about 7·2, which was confirmed by the determinations of Nillson and Pettersson (7·179) made in 1880.

[24] As the distance between, and the volumes of, the molecules and atoms of solids and liquids certainly enter into the data for the solution of the problems of molecular mechanics, which as yet has only been worked out to any extent for the gaseous state, therefore the study of the specific gravity of solids, and especially of liquids, has long since had a vast literature. With respect to solids, however, a great difficulty is met with, owing to the specific gravity varying not only with a change of isomeric state (for example, for silica in the form of quartz = 2·65, and in tridymite = 2·2) but also directly under mechanical pressure (for example, in a crystalline, cast, and forged metal), and even with the extent to which they are powdered, &c., which influences are imperceptible in liquids.

Without going into further details, we may add to what has been said above that the conception of specific volumes and atomic distances has formed the subject of a large number of researches, but as yet it is only possible to mention a few generalisations given by Dumas, Kopp, and others, which are mentioned and amplified by me in my work cited in Note 20, and in my memoirs on this subject.

1 Analogous compounds and their isomorphs have frequently nearly the same molecular volumes.

2. Other compounds, analogous in their properties, exhibit molecular volumes which increase with the molecular weight.

3. When a contraction takes place in combination in a gaseous state, then contraction is in the majority of instances also to be observed in the solid or liquid state—*that is*, the sum of the volumes of the reacting substances is greater than the volume of the resultant substance or substances.

4. In decomposition the reverse takes place to that which occurs in combination.

5. In substitution (when the volumes in a state of vapour do not vary) a very small

change of volume generally takes place—that is, the sum of the volumes of the reacting substances is almost equal to the sum of the resultant substances.

6. Hence it is impossible to judge the volume of the component substances from the volume of a compound, although it is possible to do so from the product of substitution.

7. The replacement of H_2 by sodium, Na_2, and by barium, Ba, as well as the replacement of SO_4 by Cl_2, scarcely changes the volume, but the volume increases with the replacement of Na by K, and decreases with the replacement of H_2 by Li_2, Cu, and Mg.

8. There is no foundation for comparing volumes in a solid and liquid state at the so-called corresponding temperatures—that is, at temperatures at which the vapour tension is equal in each case. The comparison of volumes at the ordinary temperature is sufficient for finding a regularity in the relations of volumes (this deduction was developed with particular detail by me in 1856).

9. Many (Perseau, Schröder, Löwig, Playfair and Joule, Baudrimont, Einhardt) have sought in vain for a multiple proportion in the specific volumes of solids and liquids.

10. The truth of the above is seen very clearly in comparing the volumes of polymeric substances. The volumes of their molecules are equal in a state of vapour, but are very different in a solid and liquid state, as is seen from the close resemblance of the specific gravities of polymeric substances. But as a rule the most complex polymerides are denser than the simpler.

11. We already know that the oxides of light metals have a less volume than the metals, whilst that of magnesium hydroxide is considerably greater, which is explained by the stability of the former and instability of the latter. In proof of this we may cite that the volume of barium (36) is greater than that of its stable hydroxide (sp. gr. 4·5, vol. 30) as well as of those of the true alkalis. The volumes of the salts of magnesium and calcium are greater than the volume of the metal, with the single exception of the fluoride of calcium. With the heavy metals the volume of the compound is always greater than the volume of the metal, and moreover, for such compounds as silver iodide, AgI ($d = 5·7$), and mercuric iodide, HgI_2 ($d = 6·2$, and the volumes of the compounds 41 and 73), the volume of the compound is greater than the sum of the volumes of the component elements. Thus the sum of the volumes Ag + I = 36, and the volume of AgI = 41. This stands out with particular clearness on comparing the volumes K + I = 71 with the volume of KI, which is equal to 54, because its density = 3·06.

12. In such kinds of combinations, between solids and liquids, as are solutions, alloys, isomorphous mixtures, and similar feeble chemical compounds, the sum of the reacting substances is always very nearly that of the resulting substance, but here the volume is either slightly larger or smaller than the original; speaking generally, the amount of contraction depends on the force of affinity acting between the combining substances.

CHAPTER XVI

ZINC, CADMIUM, AND MERCURY

THESE three metals give, like magnesium, oxides RO, which form feebly energetic bases, and like magnesium they are volatile. The volatility increases with the atomic weight. Magnesium can be distilled at a white heat, zinc at a temperature of about 930°, cadmium about 770°, and mercury about 360°. Their oxides, RO, are more easily reducible than magnesia, and mercuric oxide is the most easily reducible. The properties of their salts, RX_2, are very similar to the properties of MgX_2. Their solubility, power of forming double and basic salts, and many other qualities are in many respects identical with those of MgX_2. The greater or less ease with which they are oxidised, the instability of their compounds, the density of the metals and their compounds, their scarcity in nature, and many other properties, gradually change with the increase of atomic weight, as might be expected from the law of periodicity. Their principal characteristics, compared with magnesium, already find expression in the fact that zinc, cadmium, and mercury are heavy metals.

Zinc stands nearest to magnesium in atomic weight and in properties. Thus zinc sulphate, or white vitriol, easily crystallises with seven molecules of water, $ZnSO_4,7H_2O$. It is isomorphous with Epsom salts, and parts with difficulty with the last molecule of water; it forms double salts—for instance, $ZnK_2(SO_4)_2,6H_2O$, exactly as magnesium sulphate does.[1] *Zinc oxide*, ZnO, is a white powder, almost in-

[1] Zinc sulphate is often obtained as a bye-product—for instance, in the action of galvanic batteries containing zinc and sulphuric acid. When the anhydrous salt is heated it forms zinc oxide, sulphurous anhydride, and oxygen. The solubility in 100 parts of water at $0° = 43$, $20° = 53$, $40° = 63\frac{1}{2}$, $60° = 74$, $80° = 84\frac{1}{2}$, $100° = 95$ parts of anhydrous zinc sulphate – that is to say, it is nearly expressed by the formula $43 + 0{\cdot}52t$.

An admixture of iron is often found in ordinary sulphate of zinc in the form of ferrous sulphate, $FeSO_4$, isomorphous with the zinc sulphate. In order to separate it, chlorine is passed through the solution of the impure salt (the ferrous salt then passes into ferric), the solution is then boiled, and zinc oxide is afterwards added, which, after some time has elapsed, precipitates all the ferric oxide. Ferric oxide of the form R_2O_3 is displaced by zinc oxide of the form RO.

soluble in water,[2] like magnesia, from which, however, it is distinguished by its solubility in solutions of sodium and potassium hydroxides.[3] Zinc chloride is decomposed by water, combines with ammonium chloride, potassium chloride, &c., just like magnesium chloride.[4] Altogether the resemblance between zinc and magnesium compounds—particularly when

[2] Zinc oxide is obtained both by the combustion and oxidation of zinc, and also by the ignition of some of its salts—for instance, those of carbonic and nitric acids; it is likewise precipitated by alkalis from a solution of ZnX_2, in the form of a gelatinous hydroxide. The oxide produced by roasting zinc blende (by burning in the air when the sulphur is converted into sulphurous anhydride) contains various impurities. For purification, the oxide is mixed with water, and the sulphurous anhydride formed by roasting the blende is passed through it. Zinc bisulphite, $ZnSO_3,H_2SO_3$, then passes into solution. If a solution of this salt be evaporated, and the residue ignited, zinc oxide, free from many of its impurities, will remain.

Zinc oxide is a light white powder, used as a paint instead of *white lead*; the basic salt, corresponding with magnesia alba, is used for the same purpose (Vol. I. p. 592).

[3] For the solution of one part of the oxide 55400 parts of water are required. Nevertheless, even in such a weak solution, zinc oxide (hydroxide, ZnH_2O_2) changes the colour of red litmus paper. Zinc oxide is obtained in the wet way by adding an alkali hydroxide to a solution of a zinc salt—for instance: $ZnSO_4 + 2HKO = K_2SO_4 + ZnH_2O_2$. The gelatinous precipitate of zinc hydroxide is *soluble* in an excess of alkali, which clearly distinguishes it from magnesia. This solubility of zinc hydroxide in alkalis is due to the power of zinc oxide to form a compound, although an unstable one, with alkalis—that is to say, points to the fact that zinc oxide already partly belongs to the intermediate oxides. The oxides of the metals above-mentioned do not show this property. The property which metallic zinc itself has of dissolving in caustic alkali with the disengagement of hydrogen (the solution is facilitated by contact with platinum or iron) depends on the formation of such a compound of the oxides of zinc and the alkali metals. The solution of zinc hydroxide, ZnH_2O_2, in potash (in a strong solution), proceeds when these hydrates are taken in proportion to $ZnH_2O_2 + KHO$. If such a solution be evaporated to dryness, water extracts only caustic potash from the fused residue. When a solution of zinc hydroxide in strong alkali is mixed with a large mass of water, nearly all the oxide of zinc is precipitated; and, therefore, in weak solutions, a large quantity of the alkali is required to effect solution, which points to the decomposition of the zinc-alkali compounds by water. If strong alcohol be added to a solution of zinc oxide in sodium hydroxide, the crystallohydrate, $2Zn(OH)(ONa),7H_2O$, separates.

[4] *Zinc chloride*, $ZnCl_2$, is generally used in the arts in the form of a solution obtained by dissolving zinc in hydrochloric acid. This solution is used for soldering metals. The reason why it is thus employed is understood from its properties. When evaporated the combination with the water of crystallisation first separates, which, however, on being further heated, loses all traces of water, and forms an oily mass of anhydrous salt which solidifies on cooling. This substance melts at 250°, and commences to volatilise at about 400°. The soldering of metals—that is, the introduction of an easily-fusible metal between two contiguous metallic objects—is hindered by any film of oxide upon them; and, as heated metals easily oxidise, they are therefore difficult to solder. Zinc chloride is used to prevent the oxidation. It fuses on being heated, and, covering the metal with an oily coating, prevents contact with the air; but even if any oxide has formed, the free hydrochloric acid generally existing in the zinc chloride solution dissolves the oxide formed, and in this way the metallic surface of the metals to be soldered is preserved fit for the adhesion of the liquid solder, which, on cooling, binds the objects together. Much zinc chloride is used also for steeping wood (telegraph-posts and sleepers on railways) in order to preserve them from decaying quickly; this preservative action is in all probability mainly due to the poisonous character of zinc salts (corrosive sublimate is still

both are in solution—is so great that it exceeds the resemblance which exists between magnesium and calcium compounds.

Zinc, like many heavy metals, is often *found in nature in combination with sulphur*, forming the so-called *zinc blende*,[5] ZnS. It sometimes exists in large masses, often crystallised in cubes; it is frequently translucent, and has a metallic lustre, although this is not so clearly developed as in many other metallic sulphides with which we shall here-

more poisonous, and a still better agent to preserve wood from decay), because decay is brought about by the action of lower organisms.

The specific gravity of solutions (*see* my 'Treatise,' p. 50) containing p per cent. of zinc chloride, $ZnCl_2$:

p =	10	20	30	40	50
15°/4° =	1·093	1·184	1·293	1·411	1·554
ds/dt =	−8	−5	−7	−8	−9

The last line shows the change of specific gravity for 1° in ten-thousandth parts for temperatures near 15°. More accurate determinations of Cheltzoff, personally communicated by him, led him to conclude that solutions of zinc chloride follow the same laws as the solutions of sulphuric acid, which will be treated in Chapter XX.: (1) from H_2O to $ZnCl_2,120H_2O$ $s = S_0 + 92{\cdot}85p + 0{\cdot}1748p^2$; (2) from thence to $ZnCl_2,40H_2O$ $s = S_0 + 93{\cdot}96p - 0{\cdot}0126p^2$; (3) from thence to $ZnCl_2,25H_2O$ $s = 11481{\cdot}5 + 96{\cdot}45\ (p - 15{\cdot}89) + 0{\cdot}4567\ (p - 15{\cdot}89)^2$; (4) from thence to $ZnCl_2,10H_2O$ $s = 12212{\cdot}1 + 104{\cdot}82\ (p = 23{\cdot}21) + 0{\cdot}7992\ (p - 23{\cdot}21)^2$; (5) from thence to $p = 65$ p.c. $s = 14606{\cdot}8 + 140{\cdot}96\ (p - 43{\cdot}05) + 1{\cdot}4905\ (p - 43{\cdot}05)^2$, where s is the specific gravity of the solution at 15°, containing p p.c. of $ZnCl_2$ by weight, if the water at 4° = 10000, and where $S_0 = 9991{\cdot}6$ (specific gravity of water at 15°). The compound of zinc chloride with hydrochloric acid has been mentioned in Vol. I. page 450.

Zinc chloride has a great affinity for water; it is not only soluble in it, but in alcohol, and on being dissolved in water becomes considerably heated, like magnesium and calcium chlorides. Zinc chloride is capable of taking up water, not only in a free state, but also in chemical combination with many substances. Thus, for instance, it is used in organic researches, for removing the elements of water from many of the organic compounds.

When mixed with zinc oxide it forms with remarkable ease a very hard mass of zinc oxychloride, which is applied in the arts; for instance, in painting, to resist the action of water, or for cementing such objects as are destined to remain in water. Zinc oxychloride, $ZnCl_2,3ZnO,2H_2O (= Zn_2OCl_2,2ZnH_2O_2)$ is also formed from a solution of zinc chloride by the action of a small quantity of ammonia on it after heating the precipitate obtained with the liquid for a considerable time; the admixture of ammonium salts with a mixture of a strong solution of zinc chloride with its oxide makes a similar mass, which does not solidify so rapidly, and is therefore more useful for similar purposes. Moisture and cold do not change the hardened mass of oxychloride, and it also resists the action of many acids, and a heat of 800°, which makes it a useful cement for many purposes. A solution of magnesium chloride with magnesium oxide forms a similar oxychloride. The mass solidifies best when there is an even quantity by weight of zinc in the chloride and oxide, and, therefore, when it has the composition Zn_2OCl_2. In preparing such a cement, naturally zinc oxide alone may be taken, and the requisite quantity of hydrochloric acid added to it.

[5] This mineral has been given the name of 'mock-ore,' on account of its having the appearance (considerable density, 4·06, &c.) of ordinary metallic ores; it deceived the first miners, because it did not, like other ores, give metal when simply roasted in air and fused with charcoal. The white zinc oxide, formed by burning the vapours of zinc, was also called 'nihil album,' or 'white nothing,' on account of its lightness.

after become acquainted. The ores of zinc also comprise the carbonate, *calamine*, and silicate, *siliceous calamine*.

Metallic zinc (spelter) is most frequently obtained from the ores containing the carbonate[6]—that is, from calamine, which is sometimes found in thick veins : for instance, in Poland, Galicia, in some places on the banks of the Rhine, and in considerable masses in Belgium and England. In Russia beds of zinc ore are met with in Poland and the Caucasus ; but the output is small. In Sweden, as early as the fifteenth century, the Belgian calamine was worked up into an alloy of zinc and copper (brass), and Paracelsus produced zinc from calamine ; but the technical production of the metal itself, long ago practised in China, only commenced in Europe in 1807 in Belgium, when the Abbé Donnet discovered that zinc was volatile. From that time the production increased until it is now about 140 million kilograms in Germany alone.

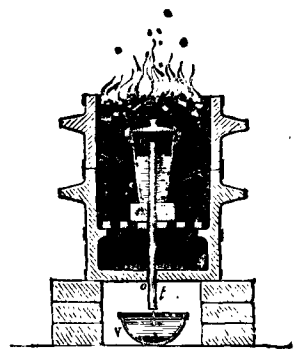

FIG. 80.—Distillation of zinc in a crucible placed in a furnace. *o c*, tubes along which the vapour passes and condenses.

The reduction of metallic zinc from its ores is based on the fact that zinc oxide[7] is easily reduced by charcoal at a red heat: $ZnO + C = Zn + CO$. The zinc thus obtained is in a finely-divided state and impure, being mixed with other metals reduced with it. The refining depends on the zinc being *converted into vapour* at a white heat, from which it easily passes into a liquid or solid state. The distillation is carried on in earthenware retorts, filled with a mixture of the divided ore and charcoal. The vapours of zinc and gases formed during the reaction escape by means of a pipe leading downwards, and are led to a space where the vapours are

[6] Let us mention here that by the word *ore* is meant a hard, heavy substance dug out of the earth, which is used in metallurgical works for obtaining the usual heavy metals long known and used. The natural compounds of sodium, or magnesium, are not called ores, because magnesium and sodium have not been long ago obtained in works. The heavy metals, those which are easily reduced and do not easily oxidise, are exclusively those which are directly applied and obtained in works. Ores either contain the metals themselves (for instance, ores of silver or bismuth), and the metals are then in a native state, or else their sulphur compounds (blende, mock-ore, pyrites—as, for instance, galena, PbS ; zinc blende, ZnS ; copper pyrites, CuFeS) or oxides (as the ores of iron), or salts (calamine, for instance). Zinc is incomparably rarer than magnesium, and is only well known because it is transformed from its ores into a metal which finds direct use in many branches of industry.

[7] Ores, when extracted from the earth by the miners, are often enriched by sorting, washing, and other mechanical operations. The sulphurous ores (and likewise others) are then generally roasted. Roasting an ore means heating it to a red heat in air. The

cooled. By this means they do not come into contact with the air, because the neck of the retort is filled with gaseous carbonic oxide, and therefore the zinc does not oxidise, otherwise its vapour would burn in the air. The vapours of zinc, entering into the cooling chamber, condense into white zinc powder or zinc dust. When the neck of the retort is heated, the zinc is obtained in a liquid state, and is cast into plates, in which form it most often enters the market.

Commercial zinc is generally impure, containing a mixture of lead, particles of carbon, iron, and other metals, carried over with the vapours, although they are not volatile at a temperature approaching 1000°. If it is required to obtain pure zinc from the commercial article it is subjected to a further distillation in a crucible with a pipe passing through the bottom, the vapours formed by the heated zinc only having exit through the pipe cemented into the bottom of the crucible. Passing through this pipe, the vapours condense to a liquid, which is collected in a receiver. Zinc thus purified is generally re-melted and cast into rods, and in this form is often used for physical and chemical researches where a pure article is required.[8]

Metallic zinc has a bluish-white colour; its lustre, compared with many other metals, is insignificant. When cast it exhibits a tabular structure. Its specified gravity is about 7—that is, varies from 6·8 to 7·2, according to the degree of compression (for instance, forging, rolling, &c.) to which it has been subjected. It is very ductile, considering its hardness. For this reason it chokes up files when being worked. Its malleability is considerable when pure, but in the ordinary impure condition in which it is sold, at the ordinary temperature it is impossible to roll it, as it breaks easily. At a temperature of 100°, however, it easily undergoes such operations, and can then be drawn into wire or sheets. If heated further it again becomes brittle, and at 200° may be even crushed into powder, so completely

sulphur then burns, and passes off in the form of sulphurous anhydride, SO_2, and the metal oxidises. The roasting is carried on in order to obtain an oxide instead of a sulphurous compound; the oxide being reducible by charcoal.

These methods, introduced ages ago, are met with in nearly all metallurgical works for nearly all ores. For this reason the preparatory treatment of zinc blende furnishes zinc oxide; this is already contained in calamine.

[8] This zinc, although homogeneous, still contains certain impurities, to remove which it is necessary to obtain some pure zinc salt and transform it into carbonate, which latter is then distilled with charcoal, and, as thin sheets of zinc can only be obtained from very pure metal, they are frequently made use of in cases where pure zinc is required. In order to remove the arsenic from zinc, it was proposed to melt it and mix it with anhydrous magnesium chloride, by which means vapours of zinc chloride and arsenic chloride are formed. Completely pure zinc is made (V. Meyer and others) by decomposing, by means of the galvanic current, a solution of zinc sulphate to which an excess of ammonia has been added.

does it lose its molecular cohesion. It melts at 433°, and distils at 930°.

Zinc does not undergo any change in the atmosphere. Even in very damp air it only becomes slowly coated with a very thin white coating of oxide. For this reason it is available for all objects which are only in contact with air. Therefore sheet zinc may be used for roofing and many other purposes.[9] This great unchangeability of zinc in the air shows its slight energy with regard to oxygen compared with the metals already mentioned, which are capable of reducing zinc from solutions. But zinc plays this part with regard to the remaining metals—for example, with reference to lead, copper, mercury, &c. Although zinc is an almost unoxidisable metal at the ordinary temperature, it burns in the air on being heated, particularly when in the form of shavings or in the condition of vapour. At the ordinary temperature zinc does not decompose water—at any rate, not if it is in a dense mass. But even at a temperature of 100° zinc begins little by little to decompose water; it easily displaces the hydrogen of acids at the ordinary temperature, and of alkalis on being heated.

In this respect, however, the action of zinc varies a great deal with the degree of its purity. Weak sulphuric acid (corresponding with the composition $H_2SO_4,8H_2O$) at the ordinary temperature does not act at all on chemically pure zinc, and even a stronger solution acts very slowly. If the temperature be raised, and particularly if the zinc be previously slightly heated, so as to cover its surface with a film of oxide, chemically pure zinc then acts on sulphuric acid. Thus, for example, one cubic centimetre of zinc in sulphuric acid, having a composition $H_2SO_4,6H_2O$, at the ordinary temperature in two hours only dissolves to the extent of 0·018 gram, and at a temperature of 100° about $3\frac{1}{2}$ grams. If we compare this slow action with that rapid evolution of hydrogen which occurs in the case of commercial zinc, we see that the influence of those impurities in the zinc is very great. Every particle of charcoal or iron introduced into the mass of the zinc, and likewise the connection of the zinc with a piece of another electro-negative metal, assists such a dissolution, as all readers of books on physics are well aware. The slowness of the action of sulphuric acid on pure zinc (and likewise on amalgamated zinc) is also explained by the fact that a layer of hydrogen is then on the surface of the

[9] Cornices and other architectural ornaments, remarkable for their lightness and beauty, are stamped out of sheet zinc. Zinc-roofing does not require painting, but it melts during a conflagration and even burns at a strong heat. Many iron vessels, &c., are covered with zinc ('galvanised') in order to prevent them from rusting.

metal, which prevents contact between the acid and the metal. The addition of cupric sulphate, or particularly a few drops of platinic chloride (the metals are reduced) to the sulphuric acid, greatly accelerates the evolution of the hydrogen, because in this case, as with commercial zinc, galvanic couples are locally formed by the copper or platinum and the zinc, under the influence of which the zinc rapidly dissolves.[10]

[10] The action of acids on metallic zinc of various degrees of purity has been the subject of many investigations particularly important with reference to the application of zinc in galvanic batteries, whilst some investigations have direct significance for chemical mechanics, although from many points the matter is not clear. I consider it useful to stop and point out those observations which I find the most complete.

Calvert and Johnson made the following series of observations on the action of sulphuric acid of various degrees of concentration on 2 grams of pure zinc during two hours. In the cold the concentrated acid, H_2SO_4, does not act, $H_2SO_4,2H_2O$ dissolves about 0·002 gram, but principally forms hydrogen sulphide, which is obtained also when the dilution reaches $H_2SO_4,7H_2O$, when 0·035 gram of zinc is dissolved. When largely diluted with water, pure hydrogen begins to be disengaged. At 130° mono- and di-hydrated sulphuric acid give sulphurous anhydride, and in two hours dissolve 0·075 and 0·142 gram of zinc. $H_2SO_4,2H_2O$ at 130° gives a mixture of hydrogen sulphide and sulphurous anhydride dissolving 0·156 gram of zinc.

Bouchardat showed that if in a vessel made of glass or sulphur dilute sulphuric acid acting on a piece of zinc liberates one part of hydrogen, then the same acid with the same piece of zinc in the same time will liberate 4 parts of hydrogen if the vessel be made of tin—that is, zinc forms a galvanic couple with tin; in a leaden vessel 9 parts of hydrogen are developed, with a vessel of antimony or bismuth 18 parts, silver or platinum 38 parts, copper 50 parts, iron 48 parts. If a salt of platinum is added to the dilute sulphuric acid (1 part of acid and 12 parts of water), Millon determined that the rapidity of the action on the zinc is increased 149 times, and by the addition of copper sulphate is rendered 45 times greater than the action of pure sulphuric acid. The salts which are added are reduced to metals by the zinc, their contact serving to promote the reaction because they form local galvanic currents.

According to the observations of Cailletet, if, at the ordinary pressure, sulphuric acid with zinc liberates 100 parts of hydrogen, then with a pressure of 60 atmospheres 47 parts will be liberated and 1 part at a pressure of 120 atmospheres. With a reduced pressure under the receiver of an air-pump 168 parts are liberated.

Helmholtz showed that a reduced pressure also exercises its influence on galvanic elements.

Debray, Löwel, Snyders, and others showed that zinc liberates hydrogen and forms basic salts and zinc oxide with solutions of many salts—for instance, MCl_n, aluminium sulphate, and alum. Sodium and potassium carbonates scarcely act, because they form a carbonate. The salts of ammonia act more strongly than the salts of potassium and sodium; the zinc remains bright. It is evident that this action is founded on the formation of double salts and basic salts.

The difference with concentration in the rate of the action of sulphuric acid on zinc (containing impurities) under otherwise uniform conditions is in evident connection with the electrical conductivity of the solution and its viscosity, although, when largely diluted, the action is almost proportional to the amount of acid in a known volume of the solution.

Forging, casting the molten metal, and similar mechanical influences change the density and hardness of zinc, and also strongly influence its power of liberating hydrogen from acids (Muhier, Behemann).

Kayander showed (1881) that when magnesium is submitted to the action of acids:

The action of zinc on acids, and the consequent formation of zinc salts, interferes with its application in many cases, particularly for the preservation of liquids either containing, or capable of developing, acid. For this reason zinc vessels ought not to be used for the preparation or preservation of food, as this often contains acids which form poisonous salts with the zinc. Even ordinary water, containing carbonic acid, slowly but surely acts on zinc.

Finally-divided zinc, or *zinc dust*, obtained in the distillation of the metal when the receiver is not heated up to the melting point, on account of its presenting a large surface of contact and containing foreign matter (particularly zinc oxide), has in the highest degree the property of decomposing acids and even water, which it easily de-

(*a*) the action depends, not on the nature of the acid but on its basicity, (*b*) the increase of the action is more rapid than the growth of the concentration, and (*c*) there is a decrease of action with the increase of the coefficient of internal friction and electrical conductivity.

Spring and Aubel (1887) measured the volume of hydrogen disengaged by an alloy of zinc and a small quantity of lead (0·6 p.c.), because the action of acids is then uniform. In order to deal with a known surface, spheres were taken (9·5 millimetres diameter) and cylinders (17 mm. dia.), the sides of which were covered with wax in order to limit the action to the end surfaces. During the commencement of the action of a definite quantity of acid the rapidity increases, attains a maximum, and then declines as the acid becomes exhausted. We annex the results for 5, 10, and 15 per cent. of hydrochloric acid. H denotes the number of cubic centimetres of hydrogen, D the time in seconds elapsing after the zinc spheres have been plunged into the acid. At 15° they obtained:

H= 50	100	200	400	600	800	1000
5 p.c. D=714	1152	1755	2731	3908	6234	15462
10 p.c. D=301	455	649	995	1573	2746	6748
15 p.c. D=106	151	233	440	826	1604	4289

At 35° they obtained:

5 p.c. D=462	705	1058	1700	2525	4132	8499
10 p.c. D= 96	148	239	460	835	1594	3735
15 p.c. D= 44	64	112	255	505	1011	2457

At 55° they obtained:

5 p.c. D=178	276	408	699	1164	2105	5093
10 p.c. D= 34	60	113	258	491	970	2457
15 p.c. D= 24	35	58	136	239	610	1593

In consequence of the complex character of the phenomenon, the authors themselves do not recognise their determinations as being absolute, and only give them a relative signification, and in this sense it is remarkable that hydrobromic acid under similar conditions (with an equivalent strength) gives a greater (from 2 to 5 times) rapidity of action than hydrochloric acid, but sulphuric acid a far less (nearly 25 times) velocity. It is also remarkable that during the reaction the metal becomes much more heated than the acid.

Let us observe that zinc dust and zinc itself, when heated with hydrated lime and similar hydrates, disengages hydrogen; this method has even been proposed for obtaining hydrogen for filling war balloons.

composes, particularly if slightly heated. On this account zinc dust is often used in laboratories and factories as a reducing agent. A similar influence of the finely-divided state is also noticed in other metals—for instance, copper and silver—which again shows the close connection between chemical and physico-mechanical phenomena. We must first of all turn to this close connection for an explanation of the widely-spread application of zinc in galvanic batteries, where the chemical (hidden, potential) energy of the acting substances is transformed into (evident, kinetic) galvanic energy, and through this latter into heat, light, or mechanical work.[10b]

Hermann and Stromeyer, in 1819, showed that *cadmium* is almost always found with zinc, and in many respects resembles it. When distilled, the cadmium volatilises sooner, because it has a lower boiling point. Sometimes the zinc dust obtained by the first distillation of zinc contains as much as 5 per cent. of cadmium. When zinc blende, containing cadmium, is roasted, the zinc passes into the state of oxide, and the cadmium sulphide in the ore oxidises into cadmium sulphate, $CdSO_4$, which fairly well resists the action of heat; therefore, if roasted zinc blende be washed with water, a solution of cadmium sulphate will be obtained, from which it is very easy to

[10b] The relation between chemical action and galvanism is so important, and has already been so much studied, and has of late years given so many new results, that this section of our science ought now to take a prominent part in theoretical (physical) chemistry. In our comparatively short and elementary course, it is not possible to touch on this question, all the more so because even at present it contains many blank spaces with reference to the comprehension of primary phenomena; for instance, the polarisation of the current and the 'transference of the ions,' evident from the disengagement of hydrogen on the copper when a piece of zinc is plunged into sulphuric acid, in which copper is in metallic contact with the zinc. However, in latter times, thanks to the experienced investigations of Hittorf, Kohlrausch, and others, and the theoretical considerations of Clausius, Thomson, and others, the mist which enveloped this region begins to lighten; still Faraday already clearly saw that the galvanic current is nothing more than a chemical movement under a changed aspect. I only consider it possible to say a few words about this subject.

From the experiments of Favre, Thomson, Berthelot, Cheltzoff, and others on the quantity of heat developed in a closed circuit, one ought to conclude that the electromotive force, or its faculty of doing a certain work E, is *proportional* to the whole quantity of heat Q produced by the reaction serving as the source of the current. If E be expressed in volts and Q in thousands of heat units referred to molecular weights, then $E = 0{\cdot}0436\ Q$. For instance, in a Daniell's element $E = 1{\cdot}09$ both by experiment and by calculation, because it must be granted that here takes place the decomposition of $CuSO_4$ into $CuO + SO_3Aq$, and the decomposition of CuO into Cu + O, together with the formation of Zn + O and $ZnO + SO_3Aq$, for which reactions $Q = 50{\cdot}18$ thousand heat units. Just the same in other primary batteries (for instance, as shown by Bunsen, Poggendorf, and others) and secondary batteries (for instance, those acting according to the reaction $Pb + H_2SO_4 + PbO_2$, as Cheltzoff showed) elements $E = 0{\cdot}0436\ Q$. The question becomes more complicated as the temperature rises, probably from the incompleteness of thermochemical determinations.

prepare metallic cadmium. Hydrogen sulphide may be used for separating cadmium from its solutions; it gives *a yellow precipitate of cadmium sulphide*, CdS (according to the equation $CdSO_4 + H_2S = H_2SO_4 + CdS$), which, on account of its characteristic colour, is used as a pigment. Cadmium sulphide, when strongly heated in air, leaves cadmium oxide, from which the metal may be obtained in precisely the same way as in the case of zinc. It should be remarked at the same time that zinc sulphate (especially in the presence of acids) does not give a precipitate of zinc sulphide with sulphuretted hydrogen, or, at all events, is only precipitated in very small quantity.

Cadmium is a white metal, and when freshly cut is almost as white and lustrous as tin. It is so soft that it may be easily cut with a knife, and so malleable that it can be easily drawn into wire, sheets, &c. Its specific gravity is 8·67, melting point 320°, boiling point 770; its vapours burn, forming a brown powder of the oxide.[11] Next to mercury it is the most volatile metal; hence Deville determined the density of its vapours compared with hydrogen, and found it to be equal to 57·1, therefore the molecule contains *one atom* whose weight = 112. V. Meyer found the like for zinc; the molecule of mercury also contains one atom (Vol. I. p. 312).

Mercury resembles zinc and cadmium in many respects, but presents that distinction from them which is always noticed in all the heaviest metals (with regard to atomic weight and density) compared with the lighter ones—namely, that it oxidises with more difficulty, and its

[11] Amongst the compounds of cadmium very closely allied to the compounds of zinc, we must mention *cadmium iodide*, CdI_2, which is used in medicine and photography. This salt crystallises very well; it is prepared by the direct action of iodine, mixed with water, on metallic cadmium. One part of cadmium iodide at 20° requires for its solution 1·08 parts of water. It may be remarked that cadmium chloride at the same temperature requires 0·71 parts of water to dissolve it, so that the iodine compound of this metal is less soluble than the chloride, whilst the reverse relation holds in the case of the corresponding compounds of the alkali or alkaline earthy metals. Cadmium sulphate crystallises well and has the composition $3CdSO_4,8H_2O$, thus differing from zinc sulphate.

Cadmium oxide is soluble, although sparingly, in alkalis, but in the presence of tartaric and certain other acids the alkaline solution of cadmium oxide does not change when boiled, whilst a *diluted* solution in that case deposits cadmium oxide; this may also serve for separating zinc compounds from those of cadmium. Cadmium is precipitated from its salts by zinc, which fact may also be taken advantage of for separating cadmium; for this reason in an alloy of zinc and cadmium, acids first of all extract the zinc. Cadmium is in all respects less energetic than zinc. Thus, for instance, it decomposes water with difficulty, and this only when strongly heated. It even acts but slowly on acids, but then displaces hydrogen from them. It is necessary here to turn attention to the fact that for alkali and alkaline earthy metals (of the even series) the highest atomic weight determines the greatest energy; but cadmium (of the uneven series), whilst having a larger atomic weight than zinc, is less energetic. The salts of cadmium are colourless, like those of zinc. De Schulten obtained a crystalline oxychloride, Cd(OH)Cl, by heating marble with a solution of cadmium chloride in a sealed tube at 200°.

compounds are more easily decomposed.[12] Besides compounds of the usual type RX_2, it also gives those of the lower type, RX, which are unknown for zinc and cadmium.[13] Mercury therefore gives salts of the composition HgX (mercurous salts) and HgX_2 (mercuric salts), the oxides having the formulæ Hg_2O and HgO respectively.

Mercury is found *in nature* almost exclusively in combination with sulphur (like zinc and cadmium, but is still rarer than them) in the form known as cinnabar, HgS. It is far more rarely met with in the native or metallic condition, and this in all probability has been derived from cinnabar. Mercury ore is found only in a few places—namely, in Spain (in Almaden), in Idria, Japan, Peru, and California. About the year 1880 Minenkoff discovered a rich bed of cinnabar in the Bahmout district (near the station of Nikitovka), in the government of Ekaterinoslav, so that now Russia even exports mercury into other countries. Mercury ores are easily reduced to metallic mercury, because the combination between the metal and the sulphur is one of but little stability. Oxygen, iron, lime, and many other substances, when heated, easily destroy the combination. If iron is heated with cinnabar, iron sulphide is formed; if cinnabar is heated with lime, mercury and calcium sulphide and sulphate are formed, $4HgS + 4CaO = 4Hg + 3CaS + CaSO_4$. On being heated in the air, or roasted, the sulphur burns, oxidises, forming sulphurous anhydride, and vapours of metallic mercury are formed. Mercury is more easily distilled than all other metals; its boiling point is about 360°, and therefore its separation from natural admixtures, decomposed by one of

[12] According to its atomic weight, mercury follows gold in the periodic system, just as cadmium follows silver or zinc follows copper:

Ni = 59	Cu = 63	Zn = 65
Pd = 106	Ag = 108	Cd = 112
Pt = 196	Au = 198	Hg = 200

Eventually we shall see the near relation of platinum, palladium, and nickel, and also of gold, silver, and copper, but we will now establish a parallel between these three groups. The relation between the physical and also chemical properties is here strikingly similar. Nickel, palladium, and platinum are very difficult to fuse (far more so than iron, ruthenium, and osmium, which stand before them). Copper, silver and gold melt far more easily in a strong heat than the three preceding metals, and zinc, cadmium, and mercury melt still more easily. Nickel, palladium, and platinum are very slightly volatile; copper, silver, and gold are more volatile; and zinc, cadmium, and mercury represent some of the most volatile metals. Zinc oxidises more easily than copper, and is reduced with more difficulty, and the same is true for mercury as compared with gold. These relations for cadmium and silver are the medium ones in the corresponding groups. Associations of a similar kind are directly conclusive of those relations which compose the essence of the law of periodicity.

[13] Thus thallium, lead, and bismuth, following mercury according to their atomic weights, form, besides compounds of the highest types TlX_5, PbX_4 and BiX_5, also the lower ones TlX, PbX_2 and BiX_3.

the above-mentioned methods, is effected at the expense of a comparatively small amount of heat. The mixture of vapours of mercury, air, and products of combustion obtained are cooled in tubes (by water or air), and the mercury condenses as liquid metal.[14]

Mercury, as everybody knows, is a liquid metal at the ordinary temperature. In its lustre and whiteness it resembles silver.[15] At $-39°$ mercury is transformed into a malleable crystalline metal, at 0° its specific gravity equals 13·596, and in the solid state at $-40°$ equals 14·39.[16] Mercury does not change in the air—that is to say, it does not oxidise at the ordinary temperature—but at a temperature approaching the boiling-point (360°), as was stated in the Introduction, it oxidises, forming mercuric oxide.

Both metallic mercury and its compounds in general produce salivation, trembling of the hands, and other unhealthy symptoms which are found in the workmen subjected to the influence of mercurial vapours or the dust of its compounds.

As many of the compounds of mercury decompose on being heated —for instance, the oxide or carbonate [17]—and as zinc, cadmium, copper,

[14] During the condensation of the vapours of mercury in works, a part forms a black mass of finely-divided particles, which give metallic mercury when worked up in centrifugal machines, or on pressure, or on further distillation. In mercury we observe a tendency to easily split up into the finest drops, which are difficult to unite into a dense mass. It is sufficient to shake up mercury with nitric and sulphuric acids in order to produce such a mercury *powder*. The mercury separated (for instance, reduced by substances like sulphurous anhydride) from solutions, forms such a powder. According to the experiments of Nernst, this disintegrated mercury when entering into reactions develops more heat than the dense liquid metal—that is to say, the work of disintegration reappears in the form of heat. This example is instructive in examining thermochemical deductions.

[15] Mercury may sometimes be obtained in quite a pure state from works (in iron bottles holding about 35 kilos), but by being used in laboratories (for baths, calibration, &c.) it absorbs impurities. Mercury may be mechanically purified in the following way: a paper filter with a fine hole (pricked with a needle) is placed in a glass funnel and mercury is poured into it, which slowly trickles through the hole, leaving the impurities upon the filter. Sometimes it is squeezed through chamois leather or through a block of wood (as in the well-known experiment with the air-pump). It may be purified from many metals by contact with dilute nitric acid, if small drops of mercury are allowed to pass through a thick layer of it (from the fine end of a funnel); or by shaking it up with sulphuric acid in air. But the complete purification of mercury for barometers and thermometers can only be attained by distillation, best in a vacuum. For this purpose Weingold's apparatus is most often used. The principle of this apparatus is very ingenious, the distillation being effected in a Torricellian vacuum continuously supplied with fresh mercury, whilst the condensed mercury is continuously removed. This process of distillation requires very little attention, and gives about one kilo. of pure mercury per hour.

[16] If the volume of *liquid* mercury at 0° be taken as 1000000, then, according to the determinations of Regnault (re-calculated by me in 1875), at t it will be $1000000 + 180{\cdot}1t + 0{\cdot}02t^2$.

[17] All salts of mercury, when mixed with sodium carbonate and heated, give mercurous

iron, and other metals separate mercury from its salts,[18] it is evident that mercury has less chemical energy than the metals already described, even than zinc and cadmium.

Nitric acid, when acting on *an excess* of mercury at the ordinary temperature, gives mercurous nitrate, $HgNO_3$.[19] The same acid, under the influence of heat and when in excess (oxide of nitrogen is separated), forms mercuric nitrate, $Hg(NO_3)_2$. This,[20] both in its composition and properties, resembles the salts of zinc and cadmium. Dilute sulphuric acid does not act on mercury, but strong sulphuric acid dissolves it, with evolution of *sulphurous anhydride* (not hydrogen), and, on being slightly heated with an excess of mercury, forms the sparingly soluble mercurous sulphate, Hg_2SO_4, but, if strongly heated with an excess of the acid, the mercuric salt, $HgSO_4$,[21] is formed. Alkalis do not act on mercury, but the non-metals chlorine, bromine, sulphur, and phosphorus easily combine with it. They form, like the acids, two series of compounds, the difference in composition being that the lower degrees contain HgX and the higher HgX_2—that is, twice as much of the haloid, or half as much mercury for the same quantity of the haloid. This shows that *mercury forms two series of compounds—mercurous*, HgX, and *mercuric*, HgX_2. The oxygen compound of the first series

or mercuric carbonates; these decompose on being heated, forming carbonic anhydride, oxygen, and vapours of mercury.

[18] According to the determinations of Thomsen, the formation of a gram of mercurial compounds from their elements develops the following amounts of heat (in thousands of units): Hg_2+O, 42; $Hg+O$, 31; $Hg+S$, 17; $Hg+Cl$, 41; $Hg+Br$, 34; $Hg+I$, 24; $Hg+Cl_2$, 63; $Hg+Br_2$, 51; $Hg+I_2$, 34; $Hg+C_2N_2$, 19. These numbers are less than the corresponding ones for potassium, sodium, calcium, barium, and for zinc and cadmium—for instance, $Zn+O$, 85; $Zn+Cl_2$, 97; $Zn+Br_2$, 76; $Zn+I_2$, 49; $Cd+Cl_2$, 93; $Cd+Br_2$, 75; $Cd+I_2$, 49.

[19] This salt easily forms the crystallo-hydrate $HgNO_3,H_2O$, corresponding with ortho-nitric acid H_3NO_4 (the terms ortho-, pyro-, and meta-acids are explained in the chapter on phosphorus), with the substitution of Hg for H. In an aqueous solution this salt can only be preserved in the presence of free mercury, otherwise it forms basic salts, which will be mentioned hereafter.

[20] Mercuric nitrate, $Hg(NO_3)_2,8H_2O$, crystallises from a concentrated solution of mercury in an excess of boiling nitric acid. Water decomposes this salt; at the ordinary temperature crystals of a basic salt of the composition $Hg(NO_3)_2,HgO,2H_2O$ are formed, and with an excess of water the insoluble yellow basic salt $Hg(NO_3)_2,H_2O,2HgO$. These three salts correspond with the type of ortho-nitric acid, $(H_3NO_4)_2$, when mercury is substituted for 1, 2 and 3 times H_2. The first salt will then be $HgH_4(NO_4)_2,6H_2O$; the second, $Hg_2H_2(NO_4)_2,H_2O$; and the third, $Hg_3(NO_4)_2,H_2O$. As all these salts still contain water, it is possible that they correspond with the tetrahydrate $=N_2O_5+4H_2O=N_2O(OH)_8$ if ortho-nitric acid $=N_2O_5+3H_2O=2NO(OH)_3$.

[21] To obtain the mercuric salt a large excess of strong sulphuric acid must be taken and strongly heated. With a small quantity of water colourless crystals of $HgSO_4,H_2O$ may be obtained. An excess of water, especially when heated, forms the basic salt (as in Note 20), $HgSO_4,2HgO$, which corresponds with trihydrated sulphuric acid, $SO_3+3H_2O=S(OH)_6$, with the substitution of H_6 by 3Hg, which in mercuric salts is equivalent to H_6.

is the suboxide of mercury, or mercurous oxide, Hg_2O, and of the second order the oxide, HgO, mercuric oxide. The chlorine compound corresponding with the suboxide is HgCl (calomel), and with the oxide corresponds $HgCl_2$ (corrosive sublimate or mercuric chloride). In the compounds HgX, mercury resembles the metals of the first group, and more especially silver—that is, the atom of mercury is here univalent, of the type RX. In the mercuric compounds there is an evident resemblance to those of magnesium, cadmium, &c., because these form compounds of the type RX_2. Here the atom of mercury is bivalent, as in the type RX_2.[22] Every soluble mercurous compound (corresponding with the type of the suboxide of mercury), HgX, forms a white precipitate of calomel, HgCl, with hydrochloric acid or a metallic chloride, because HgCl is very slightly soluble in water, $HgX + MCl = HgCl + MX$. In soluble mercuric compounds, HgX_2, hydrochloric acid and metallic chlorides do not form a precipitate, because corrosive sublimate, $HgCl_2$, is soluble in water. Alkali hydroxides precipitate the yellow mercuric oxide from a solution of HgX_2, and the black mercurous oxide from HgX. Potassium iodide forms a dirty greenish precipitate, HgI, with mercurous salts, HgX, and a red precipitate, HgI_2, with the mercuric salts, HgX_2. These reactions distinguish the mercuric salts from the mercurous salts which represent the transition from the mercuric salts to mercury itself, $2HgX = Hg + HgX_2$. The salts, HgX, as well as HgX_2, are reduced by hydrogen at the moment of separation by such metals as zinc and copper and acids, and also by many reducing agents—for example, hypophosphorous acid, as the lowest grade of oxidation of phosphorus, by sulphurous

[22] At the time when the example of such compounds as PCl_3 and PCl_5, &c., had not yet proved the variability of the valency of elements—that is, when atomicity was reckoned a fundamental and constant property of the elements—mercury was always regarded as bivalent (iron, quadrivalent; N and P, trivalent, &c.), and the mercuric compounds HgX_2 were alone taken as normal compounds of mercury, the mercurous compounds being regarded as Hg_2X_2—that is to say, that one of the affinities of each atom of mercury served for the mutual connection of the atoms of mercury which made the system Hg_2 appear bivalent. This representation may be also understood thus: the molecule HgX_2 shows the equivalency of HgX with X (according to the law of substitution), and, therefore, HgXHgX, or Hg_2X_2 was formed, as O_2H_2 is formed from OH_2. The vapour density of calomel, which indicates the molecule HgCl, was then explained by the splitting up of Hg_2Cl_2 in the vapours into two molecules, Hg and $HgCl_2$. These suppositions, at present superfluous, also suffer on account of their assuming a union between atoms of mercury, whilst in the metal itself they are separate, for the molecule of mercury contains one atom only. Besides this, experiment directly showed that the vapour density of calomel remains unchanged by the admixture of the vapours of corrosive sublimate, which would not be the case if there was only a mixture of vapours of $Hg + HgCl_2$ in the vapour of calomel, from which it must be concluded that the formula HgCl (and not Hg_2Cl_2) expresses the actual molecular weight of calomel—that is to say, that mercury is univalent in the mercurous compounds, and bivalent in the mercuric compounds.

anhydride, stannous chloride, &c. Here the mercuric salts are first transformed into the mercurous salts, and then the latter are reduced to metallic mercury. This reaction is so delicate that it serves to detect the smallest quantity of mercury. For instance, in cases of poisoning, the mercury is discovered by immersing a copper plate (particularly if a galvanic current be passed) into the solution to be tested, the mercury being then deposited upon the copper plate, which, on being rubbed, shows a silvery white colour. The copper plate, on being heated yields vapours of mercury, and then again assumes its original red colour (if it does not oxidise).

The mercurous compounds, HgX, under the action of oxidising agents, even air, pass into mercuric compounds, especially in the presence of acids (otherwise a basic salt is produced), $2HgX + 2HX + O = 2HgX_2 + H_2O$; but the mercuric compounds, when in contact with mercury, change more or less readily, and turn into mercurous compounds, $HgX_2 + Hg = 2HgX$. For this reason, in order to preserve solutions of mercurous salts, a little mercury is generally added to them.

The lowest oxygen compound of mercury—that is, *mercurous oxide*, Hg_2O—does not seem to exist, as the substance precipitated in the form of a black mass by the action of alkalis from a solution of mercurous salts gradually separates on keeping into the yellow mercuric oxide and metallic mercury, as also does a simple mechanical mixture of oxide, HgO, with mercury (Guibourt, Barfoed). The other compound of mercury with oxygen is already known to us as *mercuric oxide*, HgO, obtained in the form of a red crystalline substance by the oxidation of mercury in the air, and precipitated in the shape of a yellow powder by the action of sodium hydroxide on solutions of salts of the type HgX_2. In this case it is amorphous and more amenable to the action of various reagents (Vol. I. page 474) than when it is in the crystalline state. Indeed, on trituration, the red oxide is changed into a powder of a yellow colour. It is very sparingly soluble in water, and forms an alkaline solution which precipitates magnesia from the solution of its salts.

Mercury combines directly with chlorine, and the first product of combination is *calomel* or *mercurous chloride*, HgCl. This is obtained, as above stated, in the form of a white precipitate by mixing solutions of mercurous salts with hydrochloric acid or with metallic chlorides. A precipitate of calomel is also obtained by reducing a boiling aqueous solution of corrosive sublimate, $HgCl_2$, with sulphurous anhydride. It is likewise produced by heating corrosive sublimate with mercury. Calomel may be distilled; its vapour density equals 118 compared with

hydrogen—that is, the formula HgCl expresses its molecular composition. In the solid state its specific gravity is 7·0; it crystallises in rhombic prisms, is colourless, but has a yellowish tint, turns brown from the action of light, and, when boiled with hydrochloric acid, decomposes into mercury and corrosive sublimate. *Corrosive sublimate or mercuric chloride*, $HgCl_2$, can be obtained from or converted into calomel by many methods. An excess of chlorine (for instance, *aqua regia*) converts calomel and mercury into corrosive sublimate. It is termed corrosive sublimate on account of its being volatile, and, in medicine up to the present day, it is termed *Mercurius sublimatus seu corrosus*. The vapour density, compared with hydrogen, is 135; therefore it is more complex than calomel, as the formula shows. It forms colourless prismatic crystals of the rhombic system, boils at 303°, and is soluble in alcohol. It is usually prepared by subliming a mixture of mercuric sulphate with common salt, $HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2$. Corrosive sublimate combines with mercuric oxide, forming an oxychloride or basic salt,[23] of the composition $HgCl_2,2HgO$

[23] As feebly energetic bases (for instance, the oxides MgO, ZnO, PbO, CuO, Al_2O_3, Bi_2O_3, &c.), mercuric oxide (*see* Notes 20, 21) and mercurous oxides easily give basic salts, which are most often directly formed by the action of water on the normal salt, according to the general equation (for mercuric compounds, RX_2):

$$\underset{\text{neutral salt}}{n\mathrm{RX_2}} + \underset{\text{water}}{m\mathrm{H_2O}} = \underset{\text{acid}}{2m\mathrm{HX}} + \underset{\text{basic salt}}{(n-m)\mathrm{RX_2}m\mathrm{RO}}$$

or else are produced directly from the normal salt and the oxide or its hydroxide. Thus mercurous nitrate, when treated with water, forms basic salts of the composition $6(HgNO_3),Hg_2O,H_2O$, $2(HgNO_3),Hg_2O,H_2O$, and $3(HgNO_3),Hg_2O,H_2O$, the first two of which crystallise well. Naturally it is possible either to refer similar salts to the type of hydrates—for instance, the second salt to the hydrate $N_2O_5,4H_2O$—or to view it as a compound, $HgNO_3,HgHO$, but the contemporary budget of evidence on basic salts is not sufficiently complete to admit of generalisation. However, it is already possible to view the subject in the following aspects: (1) basic salts are principally formed from feeble bases; (2) certain metals (mentioned above) form them with particular ease, so that one of the causes of the formation of many basic salts must depend on the property of the metal itself; (3) those bases which readily form basic salts as a rule also readily form double salts; (4) in the formation of basic salts, as also everywhere in chemistry, where a sufficient quantity of facts have accumulated, we clearly see the conditions of equiponderant heterogeneous systems, such as we saw, for instance, in the formation of double salts, crystallo-hydrates, &c.

The mercuric salts (confirming the third thesis) often form double salts, and mercuric chloride easily combines with ammonia, forming $Hg(NH_4)_2Cl_4$, or in general $HgCl_2nMCl$. If a mixture of mercurous and potassium sulphates be dissolved in dilute sulphuric acid, the solution easily yields large colourless crystals of a double salt of the composition $K_2SO_4,3HgSO_4,2H_2O$. Boullay obtained crystalline compounds of mercuric chloride with hydrochloric acid, and mercuric iodide with hydriodic acid; and Thomsen describes the compound $HgBr_2,HBr,4H_2O$ as a well-crystallised salt, melting at 13°, and having, in a molten state, a specific gravity of 3·17 and a high index of refraction. Let us also mention that the power of salts for forming basic compounds has been considerably cleared up from the time of the investigations (Würtz, Lorenz, and others) of glycol, $C_2H_4(OH)_2$ (and

(magnesium and zinc form similar compounds). This compound is obtained by mixing a solution of corrosive sublimate with mercuric oxide or with a solution of sodium bicarbonate. In general, with both mercurous and mercuric salts, there is a marked tendency to form basic salts.[24]

Mercury has a remarkable power of forming very unstable compounds with ammonia, in which the mercury replaces the hydrogen, and, if a mercuric compound be taken, its atom occupies the place of two atoms of the hydrogen in the ammonia. Thus Plantamour and Hirtzel showed that precipitated mercuric oxide dried by slightly heating, when continuously heated (up to 100°–150°) in a stream of dry ammonia, leaves a brown powder of *mercuric nitride*, N_2Hg_3, according to the equation, $3HgO + 2NH_3 = N_2Hg_3 + 3H_2O$. This substance, which is attacked by water, acids, and alkalis (giving a white powder), is very explosive when struck or rubbed, evolving nitrogen, proving that the bond between the mercury and the nitrogen is very feeble.[25] By the action of liquefied ammonia on yellow mercuric oxide

polyatomic alcohols resembling it), because the ethers, $C_2H_4X_2$, corresponding with it, are capable of forming compounds containing $C_2H_4X_2nC_2H_4O$.

On the other hand, there is reason to think that the property of forming basic salts is in connection with the polymerisation of bases, especially colloidal, as developed in the chapter on silica, lead salts, and tungstic acid.

[24] Mercuric iodide, HgI_2, is obtained first as a yellow, and then as a red, precipitate on mixing solutions of mercuric salts and potassium iodide, and is soluble in an excess of the latter (in consequence of the formation of the double salt, $HgKI_3$); of ammonium chloride (for a similar reason), &c. It crystallises at the ordinary temperature in square prisms of a red colour. On being heated, these change into yellow rhombic crystals, isomorphous in crystalline form with mercuric chloride. This yellow form of mercuric iodide is very unstable, and when cooled and triturated easily again assumes the more stable red form. When fused, a yellow liquid is obtained. *Mercuric cyanide*, $Hg(CN)_2$, forms one of the most stable metallic cyanides. It is obtained by dissolving mercuric oxide in prussic acid, and by boiling prussian blue with water and mercuric oxide, ferric iron being then obtained in the precipitate. Mercuric cyanide is a colourless crystalline substance, soluble in water, and distinguishable by its great stability; sulphuric acid does not liberate prussic acid from it, and even caustic potash does not remove the cyanogen (a complex salt is probably produced), but the halogen acids disengage HCN. Like the chloride, it combines with mercuric oxide, forming the oxycyanide, $Hg_2O(CN)_2$, and it shows a very marked tendency to form double compounds—for instance, $K_2Hg(CN)_4$. The alkali chlorides and iodides form similar compounds—for instance, the salt $HgKI(CN)_2$ crystallises very well, and is produced by directly mixing solutions of potassium iodide and mercuric cyanide.

[25] The readiness with which mercuric nitride explodes shows that the connection between the nitrogen and the mercury is very unstable, and is explained by the circumstance that the so-called *mercury fulminate*, or *fulminating mercury* is an exceedingly explosive substance. This substance is prepared in large quantities for explosive mixtures; it enters into the composition of percussion caps, which explode when struck, and kindle gunpowder. Mercury fulminate was discovered by Howard, and from that time has been prepared in the following way: one part of mercury is dissolved in twelve parts of nitric acid, of sp. gr. 1·36, and when the whole of the mercury is dissolved, 5·5 parts of 90 p.c.

Weitz also obtained an explosive compound, dimercurammonium hydroxide, N_2Hg_4O, which corresponds with an ammonium oxide,

alcohol is added, and the mass is shaken. A reaction then commences, accompanied by self-heating, produced by the oxidation of the alcohol. Actually, many oxidation products are produced during the action of the nitric acid on the alcohol (glycollic acid, ethers, &c.). When the reaction becomes fairly strong, the same quantity of alcohol is added as at the commencement, and then the grey precipitate of the fulminate separates.

This salt has the composition $C_2Hg(NO_2)N$. It explodes when struck or heated. The mercury in it may be replaced by other metals—for instance, copper or zinc, and also silver. The silver salt, $C_2Ag_2(NO_2)N$, is obtained in a precisely analogous manner, and is even more explosive. Under the action of alkali chlorides, only half the silver is replaced by the alkali metal, but if the whole of the silver be replaced by an alkali metal, then the salt decomposes. This is evidently because combinations of this kind proceed in virtue of the formation of substances in which mercury, and metals akin to it, are connected in an unstable way with nitrogen. Potassium, and other light metals, are incapable of entering into such connection, and therefore, the substitution of potassium for mercury entails the splitting up of the arrangement. Investigations of the fulminates were carried on, especially by Gay-Lussac and Liebig, but only the investigations of L. N. Shishkoff fully cleared up the composition and relation of this substance to the other carbon compounds. Shishkoff showed that fulminates correspond with the nitrogen acid, $C_2H_2(NO_2)N$. The explosiveness of the group depends partly on its containing at the same time NO_2 and carbon; we already know that all such nitrogen compounds are explosive. If we imagine that the NO_2 is replaced by hydrogen, we shall have a substance of the composition, C_2H_5N. This is acetonitrile—that is, acetic acid $+NH_3-2H_2O$, or ethenyl nitrile, as shown in Chapter VI. The formation of an acetic compound by the action of nitric acid on alcohol is easily understood, because acetic acid is produced by the oxidation of alcohol, and the production of the elements of ammonia, indispensable for the formation of a nitrile, is accounted for by the fact that nitric acid, under the action of reducing substances, in many cases forms ammonia. And thus the formation of acetonitrile, C_2H_5N, becomes possible when alcohol acts on nitric acid. In this acetonitrile, an exchange of one atom of hydrogen with the group NO_2 is accomplished whilst the two others are replaced by mercury—that is to say, fulminating mercury, $C_2(NO_2)HgN$, is formed. The explosiveness of this compound is explained not only by the common presence of C_2 and NO_2, but also by the presence of Hg and N, as nitride of mercury is explosive. The presence of the group NO_2 in fulminating mercury is shown by its forming chloropicrin, $C(NO_2)Cl_3$, when treated with chlorine, similarly to other nitro compounds, and the formation of acetonitrile is demonstrated by the fact that fulminating mercury, when treated with bromine, forms bromonitroacetonitrile, $C_2(NO_2)Br_2N$. The explosiveness of fulminating mercury, the rapidity of its decomposition (gunpowder, and even guncotton, burn more slowly and explode less violently), and the force of its explosion, are such that the explosion of a small quantity (loosely covered) will shatter massive objects.

The investigations of Abel on the communication of explosion from one substance to another are remarkable. If guncotton be ignited in an open space, it burns quietly, but if fulminating mercury be exploded by the side of it, the decomposition of the guncotton is effected instantaneously, and it then shatters the objects upon which it lies, so rapid is the decomposition. Abel explains this by stating that the explosion of the fulminating salt brings the molecules of guncotton into a special, as it were, harmonious state of vibration, which engenders the rapid decomposition of the whole mass. This rapid decomposition of explosive substances establishes the distinction between explosion and combustion. Besides this, Berthelot showed that from that form of powerful molecular concussion which takes place during the explosion of fulminating mercury, the state of tension and stability of equilibrium of substances which are endothermal, or capable of decomposing with the disengagement of heat—for instance, cyanogen, nitro compounds,

$(NH_4)_2O$, in which the whole of the hydrogen is replaced by mercury. A solution of ammonia reacts with mercuric oxide, forming the hydroxide, $NHg_2{\cdot}OH$, to which a whole series of salts, NHg_2X, correspond; these are generally insoluble in water and capable of decomposing with an explosion. But salts of the same type, but with one atom of mercury, NH_2HgX, are more frequently and more easily formed; they were principally studied by Kane, although known long ago. Thus, if ammonia be added to a solution of corrosive sublimate (or, still better, in reverse order), a precipitate is obtained known as white precipitate (*Mercurius præcipitatus albus*) or *mercurammonium chloride*, NH_2HgCl, which may also be regarded as HgX_2, where one X equals Cl and the other X equals the ammonia radicle, $HgCl_2 + 2NH_3 = NH_2{\cdot}HgCl + NH_4Cl$. When heated, mercurammonium chloride decomposes, yielding mercurous chloride; when heated with dry hydrochloric acid it forms ammonium chloride and mercuric chloride. Other simple and double salts of mercurammonium, NH_2HgX, are also known.

Mercury as a liquid metal is capable of dissolving other metals and forming metallic solutions. These are generally called 'amalgams.' The formation of these solutions is often accompanied by the development of a large amount of heat—for instance, when potassium and sodium are dissolved; but sometimes heat is absorbed, as, for instance, when lead is dissolved. It is evident that phenomena of this kind are exceedingly similar to the phenomena accompanying the dissolution of salts and other substances in water, but here it is easy to demonstrate that which is far more difficult to observe in the case of salts: the solution of metals in mercury is accompanied by the formation of definite chemical compounds of the mercury with the metals dissolved. This is shown by the fact that when pressed (best of all in chamois leather) such solutions leave solid, definite compounds of mercury with metals. It is, however, very difficult to obtain them in a pure state, on account of the difficulty of separating the last traces of mercury, which is mechanically distributed between the crystals of the compounds. Nevertheless, in many cases such compounds have undoubtedly been obtained, and this is clearly shown by the evident crystalline structure and characteristic appearance of many amalgams. Thus, for instance, if about $2\frac{1}{2}$ p.c. of sodium is dissolved in mercury, a hard, crystalline amalgam is obtained, very friable and little changeable in air. It contains the compound $NaHg_5$ (Vol. I. page 529). Water decomposes

nitrous oxide, &c.—is generally destroyed. Thorpe showed that carbon bisulphide, CS_2, as an endothermal substance, also decomposes into sulphur and charcoal, when fulminating mercury is exploded in contact with it.

it, with the evolution of hydrogen, but more slowly than other sodium amalgams, and this action of water only shows that the bond between the sodium and the mercury is weak, just like the connection between mercury and many other elements—for instance, nitrogen. Mercury directly and easily dissolves potassium, sodium, zinc, cadmium, tin, gold, bismuth, lead, &c., and from such solutions or alloys it is in most cases easy to extract definite compounds—thus, for instance, the compounds of mercury and silver have the compositions HgAg and Ag_2Hg_3. Objects made of copper when rubbed with mercury become covered with a white coating of that metal, which slowly forms an amalgam; silver acts in the same way, and platinum combines with mercury with still greater difficulty. This metal only readily forms an amalgam when in the form of a fine powder. If salts of platinum in solution are poured on to an amalgam of sodium, the latter element reduces the platinum, and the platinum separated is dissolved by the mercury. Almost all metals readily form amalgams if their solutions are decomposed by a galvanic current, where mercury forms the negative pole. In this way an amalgam may even be made with iron, although iron in a mass does not dissolve in mercury. Some amalgams are found in nature—for instance, silver amalgams.

Amalgams are used in considerable quantities in the arts. Thus the solubility of silver in mercury is taken advantage of for extracting that metal from the ore by means of amalgamation, and for silvering by fire. The same may be said of gold. Tin amalgam, which is incapable of crystallising and is obtained by dissolving tin in mercury, composes the brilliant coating of ordinary looking-glasses, which is made to adhere to the surface of the polished glass by simply pressing tin sheets bathed in mercury on to the cleansed surface of the glass by mechanical means.[26]

[26] I here consider it appropriate to turn attention to the want of an element (ekacadmium) between cadmium and mercury in the periodic system (Chapter XV.). But, as in the ninth series there is not a single known element, it may be that this series is entirely composed of elements incapable of existing. However, until this is proved in one way or another, it may be concluded that the properties of ekacadmium will be between those of cadmium and mercury. It ought to have an atomic weight of about 155, to form an oxide EcO, a slightly stable oxide Ec_2O. Both ought to be feeble bases, easily forming double and basic salts. The volume of the oxide will be nearly 17·5, because the volume of cadmium oxide is about 16, and that of mercuric oxide 19. Therefore, the density of the oxide will approach 171÷17·5=9·7. The metal ought to be easily fusible, oxidising when heated, of a grey colour, with a specific volume, about 14 (cadmium=13, mercury =15), and, therefore, its specific gravity (155÷14) will nearly=11. Such a metal is unknown. But in 1879 Dahl, in Norway, discovered in the island of Oterö, not far from Kragerö, in a vein of Iceland spar in a nickel mine, traces of a new metal which he called norwegium, and which presented a certain resemblance to ekacadmium. As little ore was found, the experiments were not continued; the first information was scanty, complete

purity of the metal was not attained, and, therefore, the properties ascribed to norwegium ought to be regarded as approximate, and likely to undergo considerable alteration on further study. A solution of the roasted mineral in acid was twice precipitated by sulphuretted hydrogen, and again ignited; the oxide obtained was easily reduced. When the metal was dissolved in hydrochloric acid largely diluted with water, and the solution boiled, the basic salt was precipitated, and thus freed from the copper which remained in the solution. The reduced metal had a density 9·44, and easily oxidised. If the composition NgO be assigned to the oxide, then Ng = 145·9. It fused at 254°; the hydroxide was soluble in alkalis and potassium carbonate. In any case, if norwegium is not a mixture of other metals, it belongs to the uneven series, because the heavy metals of the even series are not easily reducible. Brauner thinks that norwegium oxide is Ng_2O_5, the atom Ng = 219, and places it in Group VI., series 11, but then the feebly acid higher oxide, NgO_3, ought to be formed.

Amongst those metals accompanying zinc which have been pointed out, but not authentically extracted, the *actinum* of Phipson must be ranked (1881). He remarked that certain sorts of zinc give a white precipitate of zinc sulphide which blackens on exposure to light and then becomes white in the dark again. Its oxide, closely resembling in many ways cadmium oxide, is insoluble in alkalis, and it forms a white metallic sulphide, blackening on exposure to light.

CHAPTER XVII

BORON, ALUMINIUM, AND THE ANALOGOUS METALS OF THE THIRD GROUP

If the elements of small atomic weight which have been as yet considered by us be placed in order, it will be clearly seen that, judging by the formulæ of their higher compounds, one element is wanting between beryllium and carbon. Indeed, lithium gives LiX, beryllium forms BeX_2, and then comes carbon, giving CX_4. Evidently to complete the series we must look for an element forming RX_3, and having an atomic weight greater than 9 and less than 12. And *boron* is such a one; its atomic weight is 11, and its compounds are expressed by BX_3.

Lithium and beryllium are metals; carbon has no metallic properties; boron appears in a free state in several forms which are intermediate between the metals and non-metals. Lithium gives an energetic caustic oxide, beryllium forms a very feeble base; hence one would expect to find that the oxide of boron, B_2O_3, has still more feeble basic properties and some acid properties, all the more as CO_2 and N_2O_5 are acid oxides. And, indeed, the only known *oxide of boron* exhibits a feeble basic character, together with the properties of a feeble acid oxide. This is even seen from the fact that a solution of boron oxide reddens blue litmus and acts on turmeric paper as an alkali, and these reactions may be used for its discovery. By themselves the alkali borates have an alkaline reaction, which clearly indicates the feeble acid character of boric acid. If they are mixed in solution with hydrochloric acid, boric acid is liberated, and if a piece of turmeric paper be immersed in this solution and then dried, the excess of hydrochloric acid volatilises, while the boric acid remains on the paper and communicates a *brown coloration* to it, just like alkalis.

Boron trioxide or boric anhydride enters into the composition of many minerals, in the majority of cases in small quantities as an isomorphous admixture, not replacing acids but bases, and most frequently (Al_2O_3) alumina, because, as a rule, the amount of alumina decreases as that of the boric anhydride increases in them. This

substitution is justified by the similarity between the atomic composition of the oxides of aluminium (alumina) and boron. The subdivision of oxides into basic and acid can in no way be sharply defined, and here we meet with the most conclusive proof of the fact, for the oxides of boron and aluminium belong to the number of intermediate oxides, closely approaching the limit separating the basic from the acid oxides. Their type (Chapter XV.) R_2O_3 is intermediate between those of the basic oxides R_2O and RO and those of the acid oxides R_2O_5 and RO_3. If we turn our attention to the chlorides, we remark that lithium chloride is soluble in water, is not volatile, and is not decomposed by water; the chlorides of beryllium and magnesium are more volatile, and although not entirely, still are decomposed by water; whilst the chlorides of boron and aluminium are still more volatile and are decomposed by water. Thus the position of boron and aluminium in the series of the other elements is clearly defined by their atomic weights, and shows us that we must not expect any new and distinct functions in these elements.

Boron was originally known in the form of sodium borate, $Na_2B_4O_7,10H_2O$, or *borax*, or *tincal*, which was exported from Asia, where it is met with in solution in certain lakes of Thibet; it has also been discovered in California and other localities.[1] Boric acid was afterwards found in sea-water and in certain mineral springs.[2] Its presence

[1] Borax is either straightway extracted from lakes (the American lakes give about 2000 tons and the lakes of Thibet about 1000), or by heating native calcium borate (see Note 2) with sodium carbonate (about 1000 tons per year), or it is obtained (up to 2000 tons) from the Tuscan impure boric acid and sodium carbonate (carbonic anhydride is evolved). Borax gives supersaturated solutions with comparative ease (Gernez), from which it crystallises, both at the ordinary and higher temperatures, in octahedra, containing $Na_2B_4O_7,5H_2O$. Its sp. gr. is 1·81. But if the crystallisation proceeds in open vessels, then at temperatures below 56°, the ordinary prismatic crystallo-hydrate $B_4Na_2O_7,10H_2O$ is obtained. Its sp. gr. is 1·71, it effloresces in dry air at the ordinary temperature, and at 0° 100 parts of water dissolve about 3 parts of this crystallo-hydrate, at 50° 27 parts, and at 100° 201 parts. Borax fuses when heated, loses its water and gives an anhydrous salt, which at a red heat fuses into a mobile liquid and solidifies into a transparent amorphous *glass* (sp. gr. 2·37), which before hardening acquires the pasty condition peculiar to common molten glass. Molten borax dissolves many oxides and on solidifying acquires the characteristic tints of these oxides; thus oxide of cobalt gives a dark blue glass, nickel a yellow, chromium a green, manganese an amethyst, uranium a bright yellow, &c. Owing to its fusibility and property of dissolving oxides, borax is employed in soldering and brazing metals. Borax frequently enters into the composition of strass and fusible glasses.

[2] We may mention the following among the minerals which contain boron: calcium borate, $(CaO)_3(B_2O_3)(H_2O)_6$, found and extracted in Asia Minor, near Brusa; *boracite* (stassfurtite), $(MgO)_6(B_2O_3)_8,MgCl_2$, at Stassfurt, in the regular system, large crystals and amorphous masses (specific gravity 2·95), used in the arts: *ereméeffite* (Damour), $AlBO_3$ or $Al_2O_3B_2O_3$, found in the Adulchalonsk mountains in colourless, transparent prisms (specific gravity 3·28) resembling apatite; *datholite*,

may be discovered by means of the green coloration which it communicates to the flame of alcohol, which is capable of dissolving free boric acid.[3] The greater portion of the boron compounds employed in the arts is obtained from the impure boric acid which is extracted in Tuscany from the so-called *suffioni*. In these localities, which present the remains of volcanic action, steam mixed with nitrogen, hydrogen sulphide, small quantities of boric acid, ammonia, and other substances, issues from the earth. Boric acid may be contained in steam, because it partially volatilises with it, and if a solution of boric acid be boiled, the distillate will always contain a certain amount of this substance.[4]

If boric acid be introduced into an excess of a strong hot solution of sodium hydroxide, then on slowly cooling the salt $NaBO_2,4H_2O$ crystallises out. This salt contains an equivalent of Na_2O to one equivalent B_2O_3 (it is BX_3 with the substitution of one X by the radicle NaO and of two X by oxygen). It might be termed a neutral salt did it not possess strongly alkaline reactions and easily split up into the alkali and the more stable borax or biborate of sodium mentioned

$(CaO)_2(SiO_2)_2B_2O_3,H_2O$. As much as 10 p.c. of boric anhydride sometimes enters into the composition of tourmaline and axinite.

[3] This green coloration is best seen by taking an alcoholic solution of volatile ethyl borate, which is easily obtained by the action of boron chloride on alcohol.

[4] How it is that these vapours containing boric acid are formed in the interior of the earth is at present unknown. Dumas supposes that it depends on the presence of *boron sulphide*, B_2S_3 (others think boron nitride), at a certain depth in the earth. This substance may be artificially prepared by heating a mixture of boric acid and charcoal in a stream of carbon bisulphide vapour, and by the direct combination of boron and the vapour of sulphur at a white heat. The almost non-crystalline compound B_2S_3 thus obtained is somewhat volatile, has an unpleasant smell, and is very easily decomposed by water, forming boric acid and hydrogen sulphide, $B_2S_3 + 3H_2O = B_2O_3 + 3H_2S$. It is supposed that a bed of boron sulphide lying at a certain depth below the surface of the earth comes into contact with sea water which has percolated through the upper strata, becomes very hot, and gives steam, hydrogen sulphide, and boric acid. This also explains the presence of ammonia in the vapours, because the sea water certainly passes through crevices containing a certain amount of animal matter, which are decomposed by the action of heat and evolve ammonia. We have, however, only mentioned this hypothesis for the sake of showing the possibility of accounting to a certain extent for the evolution of these fumes from crevices in the earth. There are several other hypotheses for explaining the presence of the vapours of boric acid, but owing to the want of other known localities the comparison of these hypotheses is at present hardly possible. The amount of boric anhydride in the vapours which escape from the Tuscan fumerolles and suffioni, as they are termed by the Italians, is very inconsiderable, less than one-tenth p.c., and therefore the direct extraction of the acid would be very uneconomical, hence the heat contained in the discharged vapours is made use of for evaporating the water. This is done in the following manner. Reservoirs are constructed over the crevices evolving the vapours, and the water of some neighbouring spring is passed into them. The vapours are caused to pass through these reservoirs, and in so doing they give up all their boric acid to the water and heat it, so that after about twenty-four hours it even boils; still this water forms only a very weak solution of boric acid. This solution is then passed into lower basins and again saturated by the vapours discharged from the

above, and which contains $2B_2O_3$ to Na_2O.[5] This salt is prepared by the action of boric acid on a solution of sodium carbonate. As borax may be perfectly purified by crystallisation, it is employed as a means for obtaining pure boric acid.

If a saturated and hot solution of borax be mixed with strong

earth, by which means a certain amount of the water is evaporated and a fresh quantity of boric acid absorbed; the same process is repeated in another reservoir, and so on until

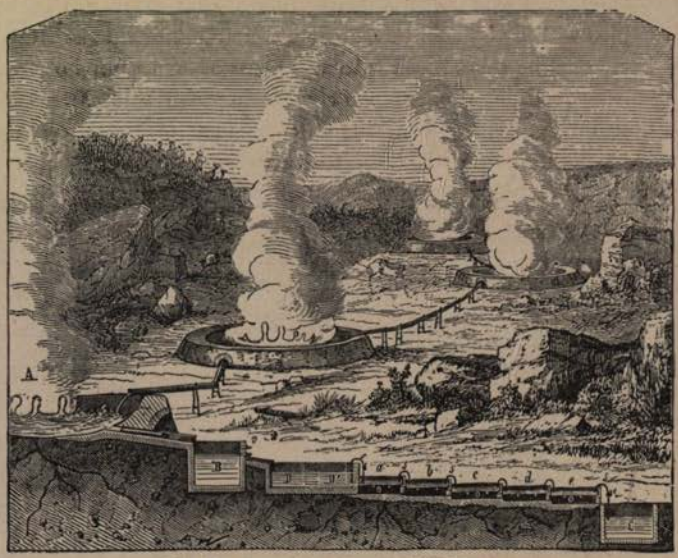

FIG. 81.—Extraction of boric acid in Tuscany.

the water has collected a somewhat considerable amount of boric acid. The solution is drawn from the last reservoir A into settling vessels B D, and then into a series of vessels *a*, *b*, *c*. In these vessels, which are made of lead, the solution is also evaporated by the vapours escaping from the earth, and attains a density of 10° and 11° Baumé. It is allowed to settle in the vessel C, in which it cools and crystallises, yielding (not quite pure) crystalline boric acid.

[5] A solution of borax, $Na_2B_4O_7$, has an alkaline reaction, decomposes ammonia salts with the liberation of ammonia (Bolley), absorbs carbonic anhydride like an alkali, dissolves iodine like an alkali (Georgiewitsch), and seems to be decomposed by water. Thus Rose showed that strong solutions of borax give a precipitate of silver borate with silver nitrate, whilst dilute solutions precipitate silver oxides, like an alkali. Georgiewitsch even supposes (1888) boric anhydride to be entirely void of acid properties, for all acids, on acting on a mixture of solutions of potassium iodide and iodate, evolve iodine, but boric acid does not do this. With dilute solutions of sodium hydroxide Berthelot obtained a development of heat equal to 11½ thousand calories per equivalent of alkali (40 grams sodium hydroxide) when the ratio $Na_2O : 2B_2O_3$ (as in borax) was taken, and only 4 thousand calories when the ratio was $Na_2O : B_2O_3$, whence he concludes that water powerfully decomposes those sodium borates in which there is more alkali than in borax. Laurent (1849) obtained a sodium compound, $Na_2O,4B_2O_3,10H_2O$, containing

hydrochloric acid, common salt and a normal crystalline hydrate of *boric acid* are formed. The composition of this hydrate is $B(HO)_3$, according to the form BX_3—that is, of the composition $B_2O_3,3H_2O$. This is the easiest method of obtaining pure boric acid. The water is easily expelled from this hydrate; it loses half at 100° and the remainder on further heating, after which the boric anhydride fuses (at 580°, according to Carnelley), forming at first a ductile (easily drawn out into threads), tenacious mass. The residual boric anhydride or trioxide of boron, B_2O_3, forms a colourless liquid when fused, which solidifies into a transparent glass, which attracts moisture from the atmosphere and then becomes cloudy.[6] Only the alkaline salts of boric acid are soluble in water, but all borates are soluble in acids, owing to their easy decomposability and the solubility of boric acid itself. Although boric anhydride, B_2O_3, absorbs $3H_2O$ from damp air, still in the presence of water it always[7] combines with a less quantity

twice as much boric anhydride as borax, by boiling a mixture of borax with an equivalent quantity of sal-ammoniac until the evolution of ammonia entirely ceased.

Hence it is evident that feeble acids are as prone to, and as easily, form acid salts (that is, salts containing much acid oxide) as feeble bases are to give basic salts. These relations become still clearer on an acquaintance with such feeble acids as silicic, molybdic, &c. This variety of the proportions in which bases are able to form salts recalls exactly the variety of the proportions in which water combines with crystallo-hydrates. But the want of sufficient data in the study of these relations does not yet permit of their being generalised under any common laws.

With respect to the feeble acid energy of boric anhydride I think it useful to add the following remarks. Carbonic anhydride is absorbed by a solution of borax, and displaces boric anhydride; but it is also displaced by it, not only on fusion, but also on solution, as the preparation of borax itself shows. Sulphuric anhydride is absorbed by boric acid, forming a compound $B(HSO_4)_3$, where HSO_4 is the radicle of sulphuric acid (D'Ally). With phosphoric acid, boric acid forms a stable compound, BPO_4, or B_2O_3,P_2O_5, undecomposable by water, as Gustavson and others have shown. With respect to tartaric acid, boric anhydride is able to play the same part as antimonious oxide. Mannitol, glycerol, and like polyhydric alcohols also seem able to form particularly characteristic compounds with boric anhydride. All these aspects of the subject require still further explanation by a method of fresh and detailed research.

[6] Ditte determined the sp. gr.:—

	0°	12°	80°
B_2O_3	1·8766	1·8476	1·6988
$B(OH)_3$	1·5463	1·5172	1·3828
Solubility	1·95	2·92	16·82

The last line gives the solubility, in grams, of boric acid, $B(OH)_3$, per 100 c.c. of water, also according to the determinations of Ditte.

[7] It is evident that, in the presence of basic oxides, water competes with them, which fact in all probability determines both the amount of water in the salts of boric acid as well as their decomposition by an excess of water. The feeble salt-forming properties of boric acid very closely resemble the similar properties of water itself. In confirmation of the above-mentioned competing action between water and bases, I think it useful to point out that the crystallo-hydrate of borax containing $5H_2O$ is composed, like $B(HO)_3$, or rather like $B_2(OH)_6$, with the substitution of one of hydrogen by sodium, because

of bases (borax only contains $\frac{1}{6}$). However, fused boric anhydride forms a crystalline compound with magnesium of the same type as the hydrate $(MgO)_3B_2O_3$ (Ebelmann), and even with sodium it forms $(Na_2O)_3B_2O_3$ or Na_3BO_3 (Benedict). As a rule, the salts of boric acid contain less base, although they are all able to form saline compounds with bases when fused. Generally, glassy fluxes are formed by this means,[8] which when fused recall ordinary aqueous solutions in many respects. Some of them crystallise on solidifying, and then they have, like salts, a definite composition. The property of boric anhydride of forming higher grades of combination with basic oxides when fused explains the power of fused borax to dissolve metallic oxides, and the remarkable experiments of Ebelmann on the preparation of artificial crystals of the precious stones by means of boric anhydride. Boric anhydride is, although difficultly, volatile at a strong heat, and therefore if it dissolves an oxide, it may be partially driven off from such a solution by prolonged and powerful ignition; in which case the oxides previously in solution separate out in a crystalline form, and frequently in the same forms as those in which they occur in nature—for example, crystals of alumina, which by itself fuses with difficulty, have been obtained in this manner. It dissolves in molten boric anhydride, and separates out in natural rhombohedric crystals. In this way Ebelmann also obtained *spinel*—that is, a compound of magnesium and aluminium oxides which is met with in nature.[9]

$Na_2B_4O_7,5H_2O = 2B_2(OH)_5(ONa)$. As the water which is held in this salt is easily parted with, so also the water of the hydrate, $B(HO)_3$, is easily parted with, and in this respect resembles water of crystallisation. These relations between boric acid, water, and bases are to a certain extent expressed by the phenomenon that molten boric anhydride dissolves bases, and leaves them behind in passing into vapour.

[8] A glass can only be formed by those little volatile oxides which correspond with feeble acids, like silica, phosphoric and boric anhydrides, &c., which themselves give glassy masses, like quartz, glacial phosphoric acid, and boric anhydride. They are able, like aqueous solutions and like metallic alloys, to solidify either in an amorphous form or to yield (or even be wholly converted into) definite crystalline compounds. This view illustrates the position of solutions amongst the other chemical compounds, and allows all alloys to be regarded from the aspect of the common laws of chemical reactions. I therefore have frequently recurred to it in this work, and introduced it since the year 1850 into various provinces of chemistry.

[9] If boric acid in its aqueous solutions proves to be exceedingly feeble, unenergetic, and easily displaced from its salts by other acids, yet in an anhydrous state, as anhydride, it exhibits the properties of an energetic acid oxide, and it *displaces* the anhydrides of other acids. This naturally does not signify that the acid then acquires new chemical properties, but only depends on the fact that the anhydrides of the majority of acids are much more volatile than boric anhydride, and therefore the salts of many acids—even of sulphuric acid—are decomposed when fused with boric anhydride.

By itself boric acid is used in the arts in small quantity, chiefly for the preservation of meat and fish (which must be afterwards well washed in water) and of milk, and for soaking the wicks of stearin candles; the latter application is based on the fact that the

Free *boron* was obtained (1809) by Davy, Gay-Lussac, and Thenard when they obtained the metals of the alkalis, because boric anhydride when fused with sodium gives up its oxygen to the sodium, and free boron is liberated as an *amorphous* powder like charcoal.[10] It is of a brown colour, and when dry does not alter in the air at the ordinary temperature; but it burns when ignited, and in so doing combines not only with the oxygen of the air, but also with the nitrogen. However, the combustion is never complete, because the boric anhydride formed on the surface covers the remaining mass of the boron, and so preserves it from the action of the oxygen. Acids, even sulphuric and phosphoric, easily oxidise amorphous boron, especially when heated, converting it into boric acid. Alkalis have the same action on it, only in this case hydrogen is evolved. Boron decomposes steam at a red heat, also with evolution of hydrogen. Amorphous boron also easily and directly combines with the metals, and with sulphur, chlorine, and nitrogen at a red heat.

Amorphous boron, like charcoal, dissolves in certain molten metals. The property of fused *aluminium of dissolving boron* in considerable quantity is very striking; on cooling such a solution the boron, partially combined with the aluminium, separates out in a crystalline form, and its properties are then exceedingly remarkable. The crystalline boron may be obtained by heating (to 1300°) the pulverulent boron with aluminium in a well-closed crucible, the access of air being prevented as far as possible. After cooling, crystals are observed on the surface of the aluminium, and may easily be separated by dissolving the aluminium in hydrochloric acid, which does not act on the crystals. The sp. gr. of the crystals is 2·68; they are partially transparent, but are mostly coloured dark brown; they contain about 4 p.c. of carbon and up to 7 p.c. of aluminium, so that they cannot be counted as pure boron. Nevertheless, the properties of this *crystalline* substance, which

wicks, which are made of cotton twist, contain an ash which is infusible by itself but which fuses when mixed with boric acid.

[10] *Amorphous boron* is prepared by mixing 100 parts of powdered boric anhydride with 50 parts of sodium in small lumps; this mixture is thrown into a powerfully-heated cast-iron crucible, covered with a layer of ignited salt, and the crucible covered. Reaction proceeds rapidly; the mass is stirred with an iron rod, and poured directly into water containing hydrochloric acid. The action is naturally accompanied by the formation of sodium borate, which is dissolved, together with the salt, by the water, whilst the boron settles at the bottom of the vessel as an insoluble powder. It is washed in water, and dried at the ordinary temperature. Magnesium, and even charcoal and phosphorus, are also able to reduce boron from its oxide. Boron, in the form of an amorphous powder, very easily passes through filter-paper, remains suspended in water, and colours it brown, so that it is considered soluble in water. Sulphur precipitated from solutions shows the same (colloidal) property.

was obtained by Wöhler and Deville, are very remarkable. It most closely resembles *the diamond in its properties*—in fact, these crystals have the lustre and high refracting power proper to the diamond only, whilst their hardness competes with that of the diamond. Their powder polishes even the diamond, and, like the diamond, scratches the sapphire and corundum. Crystalline boron is much more stable with respect to chemical reagents than the amorphous variety, and as it resembles the diamond, so amorphous boron, on the other hand, distinctly recalls certain of the properties of charcoal; thus a certain resemblance exists between boron and carbon in a free state, which is further justified by the proximity of their positions in the periodic system.

Among the other compounds of boron, those with nitrogen and the halogens are the most remarkable. As has been mentioned above, amorphous boron combines directly with *nitrogen* at a red heat. If amorphous boron be heated in a glass tube in a stream of nitric oxide, then perfect combustion takes place, $5B + 3NO = B_2O_3 + 3BN$. If the residue be treated with nitric acid, the boric anhydride dissolves, whilst the *boron nitride* remains [11] as an extremely light white powder, which is sometimes partially crystalline and greasy to the touch, like talc. It is infusible and unchanged, even at the melting-point of nickel. In general, it is remarkable for its great stability with respect to chemical reagents. Nitric and hydrochloric acids, as well as alkaline solutions, and hydrogen and chlorine at a red heat, have no action on it. When fused with potash, it evolves ammonia, and when ignited in steam it also yields ammonia: $2BN + 3H_2O = B_2O_3 + 2NH_3$.[12]

No less remarkable is the compound of boron with fluorine—*boron fluoride*, BF_3. It is produced in many instances when compounds of boron and of fluorine are brought together.[13] The most convenient

[11] At first boron nitride was obtained by heating boric acid with potassium cyanide, or other cyanogen compounds. It may be more simply prepared by heating anhydrous borax with potassium ferrocyanide, or by heating borax with ammonium chloride. For this purpose one part of borax is mixed as carefully as possible with two parts of dry ammonium chloride, and the mixture heated in a platinum crucible. A porous mass is formed, which, after crushing and treating with water and hydrochloric acid, leaves boron nitride.

[12] When fused with potassium carbonate it forms potassium cyanate, $BN + K_2CO_3 = KBO_2 + KCNO$. All this shows that boron nitride is a nitrile of boric acid, $BO(OH) + NH_3 - 2H_2O = BN$. The same is expressed by saying that boron nitride is a compound of the type of the boron compounds BX_5, with the substitution of X_3 by nitrogen, as the trivalent radicle of ammonia, NH_3.

[13] Boron fluoride is frequently evolved on heating certain compounds occurring in nature containing both boron and fluorine. If calcium fluoride is heated with boric anhydride, calcium borate and boron fluoride are formed, and the latter, as a gas, is volatilised:

method of preparing it is by heating a mixture of calcium fluoride with boric anhydride and sulphuric acid, $3CaF_2+B_2O_3+3H_2SO_4 = 3CaSO_4+3H_2O+2BF_3$.[14] It is a colourless liquefiable *gas* (the liquid boils at −100°), which on coming into contact with damp air forms white fumes, owing to its combining with water. One volume of water dissolves as much as 1050 volumes of this gas (Bazaroff), forming a liquid which disengages boron fluoride when heated, and which distils over unaltered. Boron fluoride chars organic matter, owing to its taking up the water from it, and in this respect it acts like sulphuric acid.

The behaviour of boron fluoride with water must be understood as a reversible reaction, because with water it yields hydrofluoric and boric acids, whilst they, acting on one another, re-form boron fluoride and water. A state of equilibrium is set up between these four substances (and the two reversible reactions), which is distinctly dependent on the mass of the water.[14b] When boron fluoride is in great excess, then the equilibrated system, which is capable of distilling over (sp. gr. of the liquid 1·77), has a composition $BF_3,2H_2O$ (or $B_2O_3,H_2O,6HF$). It has also its corresponding salts.[15] It is a caustic liquid, having the properties of a powerful acid; but it does not act on glass, which shows that there is no free hydrofluoric acid present. Under the action of water this system changes, with the formation of boric acid and hydroborofluoric acid (HBF_4), according to the equation $4BF_3H_4O_2=3HBF_4+BH_3O_3+5H_2O$.[16] This hydroborofluoric acid has its corresponding

$2B_2O_3+3CaF_2+2BF_3+Ca_3B_2O_6$. The calcium borate, however, retains a certain amount of calcium fluoride.

[14] The decomposition should not be carried on in glass vessels, which contain silica (in order to avoid the formation of silicon fluoride), but in lead or platinum vessels. Boron fluoride by itself does not corrode glass, but the hydrofluoric acid liberated in the reaction may bring a part of the silica into reaction. Boron fluoride should be collected over mercury, as water acts on it, as we shall see afterwards.

[14b] It appears to me that from this point of view it is possible to understand the apparently contradictory results of different investigators, especially those of Gay-Lussac (and Thenard), Davy, Berzelius, and Bazaroff.

[15] They are called fluoborates. They may be prepared directly from fluorides and borates. Such compounds of halogens with oxygen salts are known in nature (for instance, apatite and boracite), and may be artificially prepared. The composition of the fluoborates—for example, $K_3BF_3O_2$—may be expressed as that of a double salt $BO(OK),3KF$. If an excess of water decomposes them (Bazaroff), this does not signify that they do not exist, because many double salts are decomposed by water.

[16] Fluoboric acid contains boron fluoride and water, hydrofluoboric acid, boron fluoride, and hydrofluoric acid. It is evident that on the one side the competition between water and hydrofluoric acid, and, on the other hand, their power to combine, are among the forces which act here. From the fact that hydroborofluoric acid, HBF_4, can only exist in an aqueous solution, one must conclude that it forms a somewhat stable system only in the presence of $3H_2O$.

salts—for instance, KBF_4. On evaporating the aqueous solution this free acid decomposes, with the evolution of hydrofluoric acid, and a particular system is again obtained: $2HBF_4 + 5H_2O = B_2F_6H_{10}O_5 + 2HF$. The resultant solution (containing $2BF_3,5H_2O$, sp. gr. 1·58), which is identical with that formed by the evaporation of a solution of boric acid with hydrofluoric acid, again only contains a compound of boron fluoride with water. Probably there are various other possible and more or less stable states of equilibrium and definite compounds of boron fluoride, hydrofluoric acid, and water.

Nothing of this kind occurs with boron chloride, because hydrochloric acid does not act on boric acid. However, boron combines directly with chlorine at a red heat, forming *boron chloride*, BCl_3. The boron burns in the chlorine, forming a gas which, in a freezing mixture, condenses into a liquid boiling at 17°, and which gives up its excess of chlorine, if there be any, to mercury. The specific gravity of this liquid is 1·35 at 12°. Boron chloride may also be directly obtained from boric anhydride by the simultaneous action of charcoal and chlorine at a high temperature: $B_2O_3 + 3C + 3Cl_2 = 2BCl_3 + 3CO$. It is also obtained by the action of phosphoric chloride on boric anhydride in a closed tube at 200°. It is completely decomposed by water, like the chloranhydride of an acid, boric acid being formed; hence it fumes in the air: $2BCl_3 + 6H_2O = 3BH_3O_3 + 6HCl$. Boron forms with bromine a similar compound, BBr_3, boiling at 90°. The vapour densities of the fluoride, chloride, and bromide of boron, show that they contain three atoms of the halogen in the molecule—that is, that boron is a trivalent element forming BX_3.

As in the first group lithium is followed by sodium, giving a more basic oxide, so in the second group beryllium is followed by magnesium, and so also in the third group there is, besides the lightest element, boron, whose basic character is scarcely defined, *aluminium*, Al=27, whose oxide, alumina, has somewhat distinct basic properties, which, although not so powerful as in magnesium oxide, are more distinct than in boric anhydride. Among the elements of the third group, aluminium is the most widely distributed in nature; it will be enough to mention that it enters into the composition of clay to clearly see the universal distribution of aluminium in the earth's crust.

Alumina is so named from its being the metal of alums (*alumen*).

Clay, which is so widely distributed and familiar to everybody, is the insoluble residue obtained after the action of water containing carbonic acid on many rocks, and especially on the felspars contained in some of them. Felspar is a compound containing potash or soda, alumina, and silica. The primary rocks, like granite, contain many

similar compounds (*see* Chapter XVIII.: Felspars). Felspar is acted on by water containing carbonic acid, all the alkalis (potash and soda), and a portion of the silica passing into the water as substances which are soluble and carried away by it, whilst the alumina and silica left from the felspar remain on the spot where the solution has taken place. This is the original method of the formation of clay in its primary deposits among rocks along whose crevices the atmospheric water has permeated. Such primary deposits often contain a white pure clay, termed *kaolin or porcelain clay.* But such clay is a rarity, because the conditions for its formation are rarely met with. The water whilst acting chemically on rocks, at the same time destroys them *mechanically*, and carries off the finely-divided residues of disintegration with it. Clay is most easily subjected to this mechanical action of water, because it is composed of grains of exceedingly small size and void of any visible crystalline structure, which easily remain suspended in water. The cloudy water of running mountain streams generally contains particles of clay in suspension, owing to the above-described chemical and mechanical action of the water on the minerals contained in the mountain rocks. Together with these minute particles of clay the water carries away the coarser components on which it is not able to act—for example, splinters of rock matter, grains of mica, quartz, &c. They were originally held together by those minerals which form clay. When the water acts on these binding minerals, a sandy mass is formed on which water acts mechanically with great ease, and bears away the finely-divided particles with it. The cloudy water in which the particles of clay and sand are held in suspension carries them to, and deposits them at, the estuaries of rivers, lakes, seas, and oceans. The coarser particles are first deposited and form sand and like disintegrated rocky matter, whilst the clay, owing to its finely-divided state, is carried on further, and is only deposited in the still parts of the rivers, lakes, &c. Such disintegrations of rocks and separations of clay from sand have been gradually going on during the millions of years of the earth's existence, and are now proceeding, and have been the cause of the formation of the immense deposits of sandstone and clay now forming a part of the earth's strata. Such beds of clay may have been transferred by currents and streams from one locality to another, so that we must distinguish between primary and secondary deposits of clay. In places these beds of clay have, owing to long exposure under water, and perhaps partially owing to the action of heat, undergone compression, and have formed the rocky masses known as clay slates and schists, which sometimes form entire mountains. Roofing slates belong to this class of rocks.

From what has been said above it will be clear that these deposits can never consist of a chemically pure and homogeneous substance. All kinds of extraneous insoluble matter, and especially sand—that is, fragments of rock, chiefly quartz (SiO_2)—always accompany clay in a greater or less quantity and in more or less coarse particles. But it is possible to considerably purify clay from these impurities, owing to the fact that they are the result of mechanical disintegration, whilst the clay has been formed as a residue of the chemical alteration of rocky matter, and therefore its particles are incomparably more minute than the particles of sand and other rock fragments mixed with it. This difference in the size of the grains causes the clay to remain longer in suspension when shaken up in water than the coarser grains of sand. If clay be shaken up in water, and especially if it be previously boiled in it, and if after the first portion has settled the cloudy water be decanted, it will give a deposit of a very much purer clay than the original. This method is employed for purifying kaolin designed for the manufacture of the best kinds of china, earthenware, &c. A similar method is also employed in the investigation of earths for determining the *composition of soils* chiefly composed of a mixture of sand, clay, limestone, and mould. The limestone is soluble in dilute acids, but neither the clay nor sand passes into solution by this means, and therefore the limestone is easily separated in the investigation of soils. The clay is separated from the sand by a similar method to that described above, and termed *levigation.*[17]

[17] The process of *levigation* is based on the difference in the diameters of the particles of clay and sand. In density these particles differ but little from each other, and therefore a stream of water of a certain velocity can only carry away the particles of a certain diameter, whilst the particles of a larger diameter cannot be borne away by it. This is due to the resistance to falling offered by the water. This resistance to substances moving in it increases with the velocity, and therefore a substance falling into water will only move with an increasing velocity so long as the weight of the substance does not equal the resistance offered by the water, and then the movements will be uniform. And as the weight of the minute particles of clay is small, therefore the maximum velocity attained by them in falling is also small. A detached account of the theory of falling bodies in liquid, and of the experiments bearing on this subject, may be found in my work, *Concerning the Resistance of Liquids and Aeronautics*, 1880. The minute particles of clay remain suspended longer in water, and take longer to fall to the bottom, and have more difficulty in doing so. Heavy particles, although of small dimensions, fall more quickly, and are borne away by water with greater difficulty than the lighter. Thus gold and other heavy ores are washed free from sand and clay, and the coarser portions and heavy particles are left behind. A current of water of a certain velocity cannot carry away with it particles of more than a definite diameter and density, but by increasing the velocity of the current a point may be arrived at when it will bear away larger particles. A description of apparatus for the observation of phenomena of this kind is given by Schöne in his memoir in the Transactions of the Moscow Society of Natural Sciences for 1867. In order to be able to accurately vary the velocity of the current of water, a cylinder is employed in which the earth to be experimented on is placed, and water is in-

By treating clay with strong sulphuric acid, which dissolves the alumina in it; and then dissolving the silica (by means of an alkaline carbonate) combined with the alumina in the clay (but not that which occurs in the form of sand, &c.), we may form an idea of the proportion between the component parts of a clay; and by igniting it at a high temperature we may determine the amount of water held in it. In the purer sorts of clay this proportion is about $2SiO_2 : 2H_2O : Al_2O_3$.

troduced through the conical bottom of the cylinder. The rate at which the water rises in the cylinder will vary according to the quantity of water flowing per unit of time into the vessel, and consequently particles of various sizes will be carried away by the water flowing over the upper edges of the vessel. Schöne showed by direct experiment that a current of water having a velocity of 0·1 mm. per second will carry away particles having a diameter of not more than 0·0075 mm.—that is, only the most minute—with a velocity $v = 0·2$ mm. diameter $d = 0·011$ mm.; with $v = 0·3$ mm. $d = 0·0146$ mm.; with $v = 0·4$ mm. $d = 0·017$ mm.; with $v = 0·5$ mm. $d = 0·02$ mm.; with $v = 1$ mm. $d = 0·03$ mm.; with $v = 4$ mm. $d = 0·07$ mm.; with $v = 10$ mm. $d = 0·137$ mm.; with $v = 12$ mm. $d = 0·15$ mm.; and therefore if the current does not exceed one of these velocities it will only carry away or wash away particles having a diameter less than that indicated. The sand and other particles mixed with the clay will then remain in the vessel. The very minute particles obtained after levigation are all considered as clay, although not only clay but other rock matter may also exist in it as very fine particles. However, this is very seldom the case, and in reality the minute mud separated from all clays has the same composition as the purest kinds of kaolin.

The relation between the amounts of clay and sand in soils used for the cultivation of plants is very important, because a soil rich in clay is denser, heavier, shrinks up under the action of heat, and does not readily yield to the plough in dry or wet weather, whilst a soil rich in sand is friable, crumbling, easily parts with its moisture and dries rapidly, but is comparatively easily worked. Neither crumbling sand nor pure clay can be regarded as good *cultivating soils*. The difference in the amounts of clay and sand in a soil has also a purely chemical signification. Sand is easily permeated by the air, because its particles are not closely packed together. Hence the chemical change of manures proceeds very easily in sandy soils. But on the other hand such soils do not retain the nutritious principles contained in the manure, nor the water necessary for the nourishment of plants by means of their roots. Solutions of nutritious substances, containing salts of potassium, phosphoric acid, &c., when passed through sand only leave a portion moistening the surface of its particles. The sand has only to be washed with pure water and all the adhering portions of solution are washed away. It is not so with clay. If the above solutions be passed through a layer of clay the retention of the nutritive substances of these solutions will be very vigorous; this is partly because of the vast surface which the minute particles of clay expose. The nutritive elements dissolved in water are retained by the particles of clay in a peculiar manner—that is, the absorptive power of clay is very great compared to that of sand—and this has a great significance in the economy of nature. It is evident that for cultivation the most convenient soils in every respect will be those containing a definite mixture of clay and sand, and indeed the most fertile soils have this composition. The study of fertile soils, which is so important for a knowledge of the natural conditions of the introduction of fertilisers, belongs, strictly speaking, to the province of agriculture. In Russia the first foundation of a scientific fertilisation has been laid by Dokuchaeff. As an example only, we will give the composition of four soils: (1) The black earth of the Simbirsk Government; (2) a clay soil from the Smolensk Government; (3) a more sandy soil from the Moscow Government; and (4) a peaty soil from near St. Petersburg. These analyses were made in the laboratory of the St. Petersburg University about 1860, for the sake of experiments on fertilisation (conducted by me) by the Imperial Free Economical Society. 10000 grams of air-dried

In this case the conversion of felspar into kaolin is expressed by the equation : —

$$\underset{\text{Felspar.}}{K_2O,Al_2O_3,6SiO_2} = \underset{\text{Kaolin.}}{Al_2O_3,2SiO_2} + K_2O,4SiO_2 ;$$

the compound $K_2O,4SiO_2$ passes into solution.

But as a rule clays contain from 45 to 60 p.c. of silica, from 20 to 30 p.c. of alumina, and about 10 p.c. of water ; and it cannot be supposed that clays are always homogeneous, because they are an aggregation of residues (of silico-aluminous compounds) which are unacted on by water. Nevertheless, clays always contain a hydrous compound of alumina and silica, which is able to give up the alumina contained by it as a base to strong sulphuric acid, forming aluminium sulphate, which is soluble in water. After this treatment the silica remains, and is soluble in a solution of an alkaline carbonate.[18]

soil contain the following quantities (in grams) of substances capable of dissolving in acids, and of serving for the nourishment of plants.

	(1)	(2)	(3)	(4)
Na_2O	11	5	4	4
K_2O	58	10	7	5
MgO	92	33	19	7
CaO	134	17	14	11
P_2O_5	7	1	7	3
N	44	11	13	16
S	13	7	7	6
Fe_2O_3	341	155	111	46

By chemical and mechanical analysis, the chief component parts per 100 parts of air-dried soil are :

Clay	46	29	12	10
Sand	40	67	86	84
Organic matter	3·7	1·7	0·6	4·1
Hygroscopic water	6·3	1·3	0·8	1·9
Weight of a litre in grams	1150	1270	1350	960

The black earth excels the other soils in many respects.

[18] Everyone knows that a mixture of clay and water is endowed with the property of taking a given form when subjected to a moderate pressure. This peculiar property of clay renders it a precious material for practical purposes. From clay are moulded and manufactured a variety of objects, beginning with the common brick and ending with the most delicate china works of art. This *plasticity of clay* increases with its purity. The specific gravity of pure kaolin is 2·5.

When articles made of clay are dried, the well known hard mass is obtained ; but water washes it away, and furthermore, the cohesion of its particles is not sufficiently great for it to resist the impression of blows, shocks, &c. If such an article be subjected to the action of heat, its volume first decreases, then it begins to lose water, and it shrinks still further (with a continuous mass approximately by $\frac{1}{5}$ of its linear measurement). On the other hand, a great coherence of particles is obtained, and thus burnt clay has the hardness of a stone. Pure clay, however, shrinks so powerfully when burnt that the form given to it is destroyed and it easily forms cracks ; such vessels are also porous, so that they will not hold water. The addition of sand—that is, silica in fine particles—or of *chamotte*—that is, already burnt and crushed clay

Clay is the source from which alumina, Al_2O_3, and the majority of the compounds of aluminium, are prepared. Among these compounds the most important are the alums—that is, the double sulphates of potassium (and allied metals) and aluminium, $AlK(SO_4)_2,12H_2O$. When clay is treated with sulphuric acid diluted with a certain amount of water, aluminium sulphate, $Al_2(SO_4)_3$, is formed; and if potassium carbonate or sulphate is added to this solution, then potash alum is obtained in solution. The alums easily crystallise, and are prepared on a very large scale at works owing to their being employed in the process of dyeing. Alums are soluble in water, and, on the addition of ammonia to their solutions, they give *hydrous alumina*, or *aluminium hydroxide*, as a white gelatinous precipitate, which is insoluble in water but easily soluble in acids, even when dilute and in aqueous soda or potash. The solubility of alumina in acids indicates the basic character of the oxide, and its solubility in alkalis and its power of forming compounds with them shows the weakness of this basic character and the existence of an intermediate character in it. However, the feeblest acids, even carbonic acid, take up the alkali from such a solution, and the alumina then separates out in a precipitate as the hydroxide. It must also be remembered as characteristic of the salt-forming properties of alumina that it does not combine with such feeble acids as carbonic, sulphurous, or hypochlorous, &c.—that is, its compounds with these acids are decomposed by water. It is also important to mark that the hydroxide is not soluble in aqueous ammonia.

Alumina, Al_2O_3—that is, the anhydrous aluminium oxide—is met with in nature, sometimes in a somewhat pure state, having crystallised in transparent crystals, which are often coloured by impurities (chromic, cobaltic, and ferric compounds). Such are the ruby and sapphire, the former red and the latter blue. They have a specific

—renders the mass incapable of cracking in the furnace, and much more dense and less porous. Nevertheless, such clay articles (bricks, earthenware vessels, &c.) are still porous to liquids after being burnt, because the clay in the furnace is only baked and does not fuse. In order to obtain articles impervious to water the clay must either be mixed with substances which form a glassy mass in the furnace, permeating the clay and filling up its pores, or else only the surface of the article is covered with such a glassy fusible substance. In the first case the purest kinds of clay give what is known as china, in the second case porcelain or 'faïence.' So, for instance, by covering the surface of clay articles with a layer of the oxides of lead and tin, the well-known white glaze is obtained, because the oxides of these metals give a white gloss when fused with silica and clay. In the preparation of china, fluor spar and finely-ground silica is mixed up into the clay; these ingredients give a mass which is infusible but softens in the furnace, so that all the particles of the clay cohere in this softened mass, which hardens on cooling. A glaze composed of glassy substances, which only fuse at a high temperature, is also applied to the surface of china articles.

gravity 4·0, are distinguished by their very great hardness, which is only second to that of the diamond, and they represent the purest form of alumina. They are found in Ceylon and other islands of the Indian Archipelago, embedded in a rock matrix. *Corundum* is the same alumina coloured brown by a trace of oxide of iron. A very much larger proportion of this impurity occurs in *emery*, which is found in crystalline masses in Asia Minor and in Massachusetts, and which, owing to its extreme hardness, is employed for polishing stones and metals. In this anhydrous and crystalline state the aluminium oxide is a substance which very powerfully resists the action of reagents, and is insoluble both in solutions of the alkalis and of strong acids. It is only capable of passing into solution after being fused with alkalis.[19] Alumina may be obtained in this form by artificial means if the hydroxide be ignited and then fused in the oxy-hydrogen flame. By mixing different oxides with the fused mass we may obtain a transparent and coloured mass of great hardness, and resembling the natural varieties of alumina[20] in many respects. Alumina also occurs in nature in combination with water—as, for instance, in the rather rare minerals *hydrargillite* (sp. gr. 2·3), $Al_2O_3,3H_2O = 2Al(HO)_3$, and *diaspore*, $Al_2O_3,H_2O = 2AlO(HO)$ (sp. gr. 3·4). A less pure hydrate, mixed with ferric oxide, sometimes occurs in masses (at Baux, in the south of France), and is termed *bauxite*; it contains $Al_2O_3,2H_2O = Al_2O(HO)_4$ (sp. gr. 2·6). When bauxite is ignited with sodium carbonate, carbonic anhydride is liberated and the alumina then combines with the sodium oxide, forming a saline compound of the oxides of aluminium and sodium. This is taken advantage of in practice for the preparation of pure alumina compounds on a large scale, for bauxite is found in large masses (in the South of France), and the resultant compound of alumina and sodium is soluble in water and does not contain ferric oxide. This solution when subjected to the action of carbonic anhydride gives a precipitate of aluminium hydroxide,[21] which with acids forms aluminium

[19] The effects of purely mechanical subdivision on the solubility of alumina is evident from the fact that native anhydrous alumina, when converted into an exceedingly fine powder by means of levigation, dissolves in a mixture of strong sulphuric acid and a small quantity of water, especially when heated in a closed tube at 200°, or when fused with acid sulphate of potassium (*see* Vol. I. p. 541, Note 9).

[20] The preparation of crystallised alumina is given on p. 62. When alumina, moistened with a solution of cobalt salt, is ignited, it forms a blue mass called Thenard's salt. This coloration is not only taken advantage of in the arts, but also for distinguishing alumina from other earthy substances resembling it.

[21] The treatment of bauxite is carried on on a large scale, chiefly to obtain alumina from alkaline solutions, free from ferric oxide, because in dyeing it is necessary to have salts of alumainium which do not contain iron. But this end, it would seem, may be also

salts. If aqueous ammonia be added to a solution of aluminium sulphate a gelatinous precipitate is formed, which at first remains suspended in the liquid, and then on settling forms a gelatinous mass, which itself indicates the *colloidal property of aluminium hydroxide.* The following points are characteristic of this colloidal state: (1) in an anhydrous state such a colloidal substance is insoluble in water, as alumina is; (2) in the hydrated state, it is gelatinous and insoluble in water; and (3) it is also capable of appearing in solutions, from which it separates out in a non-crystalline state, forming a substance resembling glue. These different states of colloids were distinguished by Graham, who gave them the following very characteristic names. He called the gelatinous form of the hydrate *hydrogel, i.e.* a gelatinous hydrate, and the soluble form of the aqueous compound, *hydrosol,* from the Latin for a soluble hydrate. Alumina readily and frequently assumes these states. The gelatinous hydrate of alumina is its hydrogel. It is, as has been already mentioned, insoluble in water, and, like all similar hydrogels, shows not the faintest sign of crystallisation; it easily varies in many of its properties with the amount of water it contains, and loses its water on ignition, leaving a white powder of the anhydrous oxide. The hydrogel of alumina is soluble in both acids and alkalis. It may also be obtained by the evaporation of its solutions in such feebly energetic acids as volatile acetic acid. These properties are very frequently made use of in the arts, and especially in *the processes of dyeing,* because the hydrogel of alumina in precipitating attracts a number of colouring matters from their solutions, the precipitate being thus coloured by the dyes attracted.[22]

obtained by igniting alumina containing ferric oxide in a stream of chlorine mixed with hydrocarbon vapours, because ferric chloride then volatilises. K. Bayer observed that in the treatment of bauxite with soda, about 4 molecules of sodium hydroxide pass into solution to 1 molecule of alumina, and that on agitating this solution (especially in the presence of some already precipitated aluminium hydroxide), about two-thirds of the alumina is precipitated, so that only 1 molecule of alumina to 12 molecules of sodium hydroxide remains in solution. This solution is straightway evaporated, and again used. In the ignition of sodium carbonate with bauxite, the carbonic anhydride is only completely liberated when a mixture is made in the ratio $Na_2CO_3 : Al_2O_3$. But, in dissolving, it is best to further add 2 molecules of sodium hydroxide, because otherwise a portion of the alumina remains with the ferric oxide. The hydroxide, which separates from the alkaline solution, contains $Al(OH)_3$. All these relations bear a great resemblance to those of boric acid. One must imagine that the relation between sodium hydroxide and alumina in solution varies with the mass of water.

If lime be added to a solution of alumina in alkali (sodium aluminate) then calcium aluminate is precipitated, from which acids first extract the lime, leaving aluminium hydroxide, which is easily soluble in acids (Loewig). When sodium aluminate is mixed with a solution of sodium bicarbonate, a double carbonate of the alkali and aluminium is precipitated, which is easily soluble in acids.

[22] These coloured precipitates of alumina are termed *lakes,* and are employed in dyeing tissues and in the formation of various pigments—such as pastels, oil colours, &c.

The preparation of fixed dyes and the employment of aluminous compounds in the processes of dyeing is founded on this fact. When precipitated upon the fibres of tissues (cloths, linens, &c.) the aluminium hydroxide renders them impermeable to water; this may be taken advantage of for the preparation of waterproof tissues.

In dye-works the aluminium acetate is generally obtained in solution by taking a solution of alum, which is mixed with a solution of lead acetate. In this case lead sulphate is precipitated and aluminium acetate remains in solution, together with either acetate or sulphate of potassium, according to the amount of acetate of lead first taken. The complete decomposition will be as follows: $KAl(SO_4)_2 + 2Pb(C_2H_3O_2)_2 = KC_2H_3O_2 + Al(C_2H_3O_2)_3 + 2PbSO_4$, or the less complete decomposition, $2KAl(SO_4)_2 + 3Pb(C_2H_3O_2)_2 = 2Al(C_2H_3O_2)_3 + K_2SO_4 + 3PbSO_4$.[23] If the resultant solution of aluminium acetate be

Thus, if organic colouring matters, such as logwood, madder, &c., are added to a solution of any aluminium salt, and then an alkali is added, so that alumina may be precipitated, these pigments, which are by themselves soluble in water, will come down with the precipitate. This shows that alumina is able to combine with the colouring matter, and that this compound is not decomposed by water. The dyes then become insoluble in water. If a dye be mixed with starch paste and aluminium acetate, and then, by means of engraved blocks having a design in relief, we transfer this design to a material, and the material be heated, then the aluminium acetate will leave the hydrogel of alumina which binds the colouring matter, and water will no longer be able to wash the pigment from the material —that is, a so-called 'fixed' dye is obtained. In the case of dyeing a material a uniform tint, it is first soaked in a solution of aluminium acetate and then dried, by which means the acetic acid is driven off, while the hydrogel of alumina adheres to the fibres of the material. If the material is then passed through a solution of a dye in water, the former will be attracted to the portions covered with alumina, and closely adhere to them. If certain parts of the material be protected by the application of an acid, such as tartaric, $C_4H_6O_6$, oxalic, citric, &c. (these acids are non-volatile), then the alumina will be dissolved in those parts, and the pigment will not adhere, so that after washing a white design will be obtained on those parts which have been protected by the acid.

[23] As the salt of potassium obtained in the solution passes away with the water used for washing, and the salt of lead precipitated has no practical use, this method for the preparation of aluminium acetate cannot be considered an economical one; it is retained in the process of dyeing mainly because both the salts, alum and sugar of lead, employed easily crystallise, it being easy to judge their degree of purity in this form. Indeed, it is very important to employ pure reagents in dyeing, because if impurity is present—such as a small quantity of an iron compound—the tint of the dye changes; thus madders give a red colour with alumina, but if oxide of iron be present the red changes into a violet tint. The aluminium hydroxide is soluble in alkalis, whilst ferric oxide is not. Therefore sodium aluminate—that is, the dissolved compound of alumina in caustic soda—obtained, as has been described, from bauxite, is sometimes employed in dyeing. Another direct method for the preparation of pure aluminium compounds consists in the treatment of *cryolite* containing aluminium fluoride together with sodium fluoride, $AlNa_3F_6$. This mineral is exported from Greenland, and is also found in the Urals. It is crushed and heated in reverberatory furnaces with lime, and the resultant mass is treated with water; sodium aluminate is then obtained in solution, and calcium fluoride in the precipitate $AlNa_3F_6 + 3CaO = 3CaF_2 + AlNa_3O_3$. Every aluminium salt gives a solution containing sodium aluminate free from iron, when it is mixed with excess of caustic soda. This

evaporated or further boiled, then the acetic acid passes off and the hydrogel of alumina remains.

The hydrosol of alumina—*i.e.* the soluble aluminium hydroxide—is more difficult to obtain.[24] In order to obtain this soluble variety of alumina, Graham took a solution of its hydrogel in hydrochloric acid—that is, a solution of aluminium chloride, which is able to dissolve a still further quantity of the hydrogel of alumina, forming a basic salt having probably one of the compositions $Al(HO)Cl_2$ or $Al(HO)_2Cl$. When such a solution, considerably diluted with water, is subjected to dialysis—that is, to diffusion through a membrane[25]—the hydrochloric acid diffuses through the membrane and leaves the alumina in the form of hydrosol. The resultant solution, even when only containing two or three per cent. of alumina, passes into the hydrogel state with such facility that it is sufficient to transfer it from one vessel to another which has not been previously washed with water, for the entire mass to solidify into a jelly. But a solution containing not more than half a per cent. of alumina may even be boiled without coagulating; however, after the lapse of several days this solution will of its own accord yield the hydrogel of alumina. The most remarkable peculiarity of Graham's solution is that it solidifies on litmus paper, and leaves a blue ring on it, which shows the alkaline—that is, basic—character of the alumina in such a solution. If in the dialysis the

solution, when mixed with a solution of ammonium chloride, gives a precipitate of the hydrogel of alumina: $Al(OH)_3 + 3NaHO + 3NH_4Cl = Al(OH)_3 + 3NaCl + 3NH_4OH$. There was originally free soda, and on the addition of sal-ammoniac there is free ammonia, and this does not dissolve alumina, therefore, the hydrogel of the latter is precipitated.

[24] Crum first prepared a solution of basic acetate of alumina—that is, a salt containing as large as possible an excess of aluminium hydroxide with as small as possible a quantity of acetic acid. The solution must be dilute—that is, not contain more than one part of alumina per 200 of water—and if this solution be heated in a closed vessel (so that the acetic acid cannot evaporate) to the boiling point of water, for one and a half to two days, then the solution, which apparently remains unaltered, loses its original astringent taste, proper to solutions of all the salts of alumina, and has instead the purely acid taste of vinegar. The solution then no longer contains the salt, but acetic acid and the hydrosol of alumina in an uncombined state; they may be isolated from each other by evaporating the acetic acid in shallow vessels at the ordinary temperature, and with a thin layer of liquid the alumina does not separate as a precipitate. When the acid vapours cease to come off there remains a solution of the hydrosol of alumina, which is tasteless and has no action on litmus paper. When concentrated, this solution acquires a more and more gluey consistency, and when entirely evaporated over a water-bath it leaves a non-crystalline glue-like hydrate, whose composition is $Al_2H_4O_5 = Al_2O_3{,}2H_2O$. The smallest quantity of alkalis, and of many acids and salts, will convert the hydrosol into the hydrogel of alumina—that is, convert the aluminium hydroxide from a soluble into an insoluble form, or, as it is said, cause the hydrate to coagulate or gelatinise. The smallest amount of sulphuric acid and its salts will cause the alumina to gelatinise—that is, cause the hydrogel to separate. Many such colloidal solutions are known (Vol. I. p. 98, Note 54).

[25] In a dialyser, Vol. I. p. 69, Note 18.

basic chloride be replaced by a similar acetate, a hydrosol of alumina is obtained which does not act on litmus.

The different states in which the hydrates of alumina occur and are prepared resemble similar varieties of the hydrates of the oxides of iron and chromium, of molybdic and tungstic acids, as well as of phosphoric and silicic acids, of many sulphides, proteïd substances, &c. We shall therefore have occasion to recur to this subject in the further course of this work.

With respect to alumina as a base, it is very important to observe that it is not only capable of combining with other bases [26] but that it does not give salts with feeble volatile acids (like carbonic and hypochlorous); it forms salts which are easily decomposed by water, especially when heated,[27] as well as double and basic salts,[28] *so that it forms a clear example of a feeble base.*[29] To these characteristics of alumina we must add that it not only gives compounds of the type

[26] Compounds of alumina with bases (aluminates, *see* Note 21) are sometimes met with in nature. Such are spinel (*see* p. 62), $MgO,Al_2O_3 = MgAl_2O_4$, chrysoberyl, $BeAl_2O_4$, and others. Magnetic oxide of iron, $FeO,Fe_2O_3 = Fe_3O_4$, and compounds like it, belong to the same class. Here we evidently have a case of combination 'by analogy,' as in solutions and alloys, accompanied by the formation of strictly definite saline compounds, and such instances form a clear transition from so-called solutions and certain mixtures to the type of true salts. From this aspect, which I long ago introduced, many sides of chemical relations become considerably clearer.

[27] Not only aluminium acetate (Note 24), but also every other aluminium salt with a volatile acid, parts with its acid on heating an aqueous solution—that is, is decomposed by water. By dissolving aluminium hydroxide in nitric acid we may easily obtain a well-crystallising *aluminium nitrate*, $Al(NO_3)_3,9H_2O$, which fuses at 73° without decomposing (Ordway), gives a basic salt, $2Al_2O_3,6HNO_3$, at 100°, and at 140° leaves the aluminium hydroxide perfectly free from the elements of nitric acid. But the solutions of this salt, like those of the acetate, are also able to yield aluminium hydroxide. From all this it is evident that we must suppose the solutions of this and like salts to contain an equilibrated dissociated system, containing the salt, the acid, and the base, and their compounds with water, as well as partly the molecules of water itself. Such examples much more clearly confirm those conceptions of solutions which are given in the first chapter than a general preliminary acquaintance with the subject can do.

[28] Many double salts, especially silicates—like the orthoclases, micas, &c., cryolite (Note 23), &c.—as well as basic salts, are met with in nature, and are easily formed in a number of cases. As an example of native basic salts we may cite *alunite*, or alum-stone (sp. gr. 2·6), which sometimes occurs in crystals, but more frequently in fibrous masses. It has been found in masses in the Caucasus, and in Western Europe the locality of Tolfa, near Rome, is known. Its composition is $K_2O,3Al_2O_3,4SO_3,6H_2O$ (aluminite contains $9H_2O$). It is soluble in water, but not decomposed by it, but after being slightly ignited it gives up alum to it. It may be artificially prepared by heating a mixture of alum with aluminium sulphate in a closed tube at 230°.

[29] As the colloidal properties are particularly sharply developed in those oxides (Al_2O_3, SiO_2, MoO_3, SnO_2, &c.) which show (like water also) the properties of feeble bases and feeble acids, there is probably some causal reason for this coincidence, all the more so as among organic substances—gelatins, albumins, &c.—the representatives of the colloids also have the property of feebly combining with bases and acids (*see* the following chapter on silica).

AlX_3, but also the polymeric type Al_2X_6, even when X is a simple univalent haloid like chlorine. Deville and Troost showed (1857) that the vapour density of aluminium chloride (about 400°) is 9·37 with respect to air—that is, nearly 135 with respect to hydrogen—and therefore the weight of its molecule is expressed by Al_2Cl_6, and not $AlCl_3$,[30] although in the case of boron, arsenic, and antimony, which

[30] Since Deville's experiments the question of the density of aluminium chloride has been frequently recurred to. The subject has more especially occupied the attention of Nilson, Pettersson, Friedel and Crafts, and V. Meyer and his collaborateurs. In general, it has been found that at low temperatures (up to 440°) the density is constant, and indicates a molecule Al_2Cl_6; whilst depolymerisation probably (although it is not yet certain) takes place at higher temperatures, and the molecule $AlCl_3$ is obtained. Along with this there has been, and is now, a difference of opinion as to the vapour density of aluminium ethyl and methyl—for instance, as to whether $Al(CH_3)_3$ or $Al_2(CH_3)_6$ expresses the molecule of the latter. The interest of these researches is intimately connected with the question of the valency of aluminium, if we hold to the opinion (which is quite foreign to the author of this work) that elements in their corresponding compounds have a constant and strictly definite valency. In this case the molecule $AlCl_3$, or $Al(CH_3)_3$, would show that Al is trivalent, and consequently the compounds of aluminium are $Al(OH)_3$, AlO_3Al, and, in general, AlX_3. But if the molecule be Al_2Cl_6, then it is not compatible—for the followers of the doctrine of the invariable valency of the elements—with the idea of the trivalency of aluminium, and they recognise it to be quadrivalent like carbon by likening Al_2Cl_6 to ethane $C_2H_6 = CH_3CH_3$, although this did not explain why Al does not form $AlCl_4$, or, in general, AlX_4. In this work another representation is introduced and, according to it, although aluminium, as an element of Group III., gives compounds of the type AlX_3, still this does not exclude the possibility of these molecules combining with others, and consequently with *each other*—that is, forming Al_2X_6; just as the molecules of univalent elements appear as H_2, or as Na, and the molecules of bivalent elements as Zn, or as S_2, or even S_6. It would be strange to ask whether mercury as vapour is uni- or bi-valent? does it correspond with HgX, or HgX_2? Evidently, neither one nor the other. Before all it must be seen that the limiting form does not exhaust all power of combination, it only exhausts the capacity for combination with those X's, but the saturated substance may afterwards combine with *whole molecules*, which fact is best proved by the capacity of substances to form crystalline compounds with water, ammonia, &c. But in some substances this faculty for further combinations is not well developed (for instance, carbon tetrachloride, CCl_4), and in others more so. AlX_3 combines with many other molecules. If a limiting form, which does not combine with new X's, combines, however, with other whole molecules, then it will naturally in some instances combine with itself, will polymerise. In this manner the mind clearly grasps that those forces which cause S_2 to unite itself to Cl_2, or C_2H_4 to Cl_2, &c., also unite molecules of a similar kind together; thus *polymerisation* ceases to be an isolated fragmentary phenomenon, and chemical combinations 'by analogy' receive a particular and important interest. In conformity to these views the following conclusion may be made concerning the compounds of aluminium. They are of the type AlX_3 in the limit, like BX_3, but those limiting forms are still able to combine to form AlX_3,RZ, and the aluminium chloride is a compound of this kind—*i.e.* $(AlX_3)_2$. In boron, in BCl_3, this faculty to form further compounds is less developed. Hence it appears as BCl_3, and not $(BCl_3)_2$. This is clearly proved in reality. We shall see that aluminium chloride gives a compound with many other chlor-anhydrides. Polymerisation is not only possible when a substance has not attained the limit (although it is more probable then), but also when the limiting form has been formed, if only the latter has the faculty of combining with other whole molecules. Therefore we may conclude that aluminium, like boron, is trivalent if lithium and sodium are univalent, magnesium bivalent, and carbon tetravalent. In a word, there is no

give oxides R_2O_3 of the same composition as Al_2O_3, the chlorine compounds form non-polymeric molecules, BCl_3, $AsCl_3$, $SbCl_3$.[31] This duplication (polymerisation) of the form AlX_3 is connected with the facility with which the salts of aluminium combine with other salts to form double salts, and with aluminium hydroxide itself to form basic salts.

Aluminium sulphate, $Al_2(SO_4)_3$, which is obtained by treating clay or the hydrates of alumina with sulphuric acid, crystallises in the cold with $27H_2O$, or at the ordinary temperature in pearly crystals, which are greasy to the touch and contain $16H_2O$.[32] Its solutions act like sulphuric acid—for instance, evolve hydrogen with zinc, forming basic salts, which are sometimes met with in nature (*aluminite*, $Al_2O_3,SO_3,9H_2O$, *alumiane*, $Al_2O_3,2SO_3$, and others), which may be obtained by the decomposition of normal salts and by the direct solution of the hydroxide in normal salts : these exhibiting a varying composition, $(Al_2O_3)_n(SO_3)_m(H_2O)_q$, where m/n is less than 3. With solutions of the alkali sulphates (potassium, sodium, ammonium, rubidium, and cæsium sulphates), the normal salt easily forms double salts, termed *alums*—for example, the ordinary crystalline alum contains $KAl(SO_4)_2,12H_2O$, or $K_2SO_4,Al_2(SO_4)_3,24H_2O$. In the ammonium alums (which leave a residue of alumina when ignited) the potassium is replaced by ammonium (NH_4). Alums are used in large quantities, because there is scarcely any other salt which crystallises so easily as the last-mentioned. In this respect the alums formed by potassium and ammonium are equally convenient to purify, because they present a considerable difference in their solubility at the ordinary and higher temperatures. If the deposition be conducted rapidly, the salt separates in minute crystals, but if it be slowly deposited, especially in large masses, as at works, then crystals several centimetres long are

reason to consider that aluminium is capable of forming compounds AlX_4, and in this manner to explain the existence of the molecule Al_2Cl_6. The fact that it exists, together with the existence of AlX_3, and perhaps of even $AlCl_3$, is one of the indications of the insufficiency of the doctrine of an invariable valency of the elements as their fundamental property (Note 31).

Furthermore, there are many reasons for thinking that AlF_3, Al_2O_3, and other empirical formulæ do not express the molecular weight of these compounds, but that it is much higher: Al_nF_{3n}, $Al_{2n}O_{3n}$.

[31] In the case of gallium, as a close analogue of aluminium, Lecoq de Boisbaudran (1880) showed that probably the molecule gallium chloride contains Ga_2Cl_6 at low temperatures and high pressures, and that it dissociates into $GaCl_3$ at high temperatures and low pressures. According to the observations of the investigators given in Note 30, the molecule of indium chloride seems to appear in the simplest form, $InCl_3$, and does not polymerise (*see* Note 30).

[32] The pure salt ($16H_2O$) is not hygroscopic. In the presence of impurities the amount of water increases to $18H_2O$, and the salt becomes hygroscopic.

sometimes obtained. At a higher temperature alums are very much more soluble, and crystallise with greater difficulty, and are therefore less easily freed from impurities; at 0° 100 parts of water dissolve 3 parts, at 30° 22 parts, at 70° 90 parts, and at 100° 357 parts of potassium alum.[33] The solubility of ammonium alum is slightly less. The specific gravity of potassium alum is 1·74, of ammonium alum 1·63, and of sodium alum 1·60. Alums easily part with their water of crystallisation; thus potash alum partially effloresces when exposed to the air, and loses 9 mol. H_2O under the receiver of an air-pump. At 100° dry air, if passed over alums, takes up nearly all their water. As we have already mentioned (Chap. XV.), the law of isomorphous substitutions evinces itself more clearly in the alums than in any other salts, and all alums not only contain an equal amount of water of crystallisation, $MR(SO_4)_2 12H_2O$, where M=K, NH_4, Na, R=Al, Fe, Cr, and not only appear in crystals whose planes are inclined at equal angles, but they also give every possible kind of isomorphous mixture. The aluminium in them is easily replaced by iron, chromium, indium, and partly by others, whilst the potassium may be substituted by sodium, rubidium, ammonium, and thallium, and the sulphuric acid may be replaced by selenic and chromic acids.

Aluminium chloride, Al_2Cl_6, is obtained, like the other similar chlorides, either directly from chlorine and the metal, or by heating to redness an intimate mixture of the amorphous anhydrous oxide and charcoal in a stream of chlorine. The resultant sublimate is very volatile,[34] and forms a crystalline, easily-fusible mass, which deliquesces in the air and easily dissolves in water, with the evolution of a large amount of heat. In this respect aluminium chloride resembles the chlor-anhydrides of the acids, and probably in the aqueous solution the elements of the hydrochloric acid are already separated, at least partially, from the aluminium hydroxide. The solution may also be obtained by the action of aluminium hydroxide on hydrochloric acid. On evaporating this solution, hydrochloric acid and aluminium hydroxide are liberated. But with an excess of hydrochloric acid, and if the solution be heated in a closed tube, then on cooling crystals of

[33] The common form of crystals of alums is octahedral, but if this solution contains a certain small excess of alumina above the ratio $2Al(OH)_3$ to K_2SO_4, and not more sulphuric acid than $3H_2SO_4$ to $2Al(OH)_3$, then it easily forms combinations of the cube and octahedron, and these alums are called 'cubic' alums. They are valued by the dyer because they can contain no iron in solution, for oxide of iron is precipitated before alumina, and if the latter be in excess there can be no oxide of iron present. These alums were long exported from Italy, where they were prepared from alunite (Note 28).

[34] Aluminium chloride fuses at 178°, boils at 183° (pressure 755 mm., at 168° under a pressure of 250 mm., and at 213° under 2278 mm.), according to Friedel and Crafts.

$AlCl_3,6H_2O$ are obtained—that is, aluminium chloride both combines with water and is decomposed by it. And the faculty of the type AlX_3 for combining with other molecules is seen in the compounds of $AlCl_3$ with many other chlorine compounds. So, for example, a mixture of aluminium chloride with sulphur tetrachloride gives Al_2Cl_6,SCl_4 under the action of chlorine, whilst with phosphorus pentachloride it forms $AlCl_3,PCl_5$; it also combines with NOCl. In all such compounds it is not Al_2Cl_6 which enters into their composition, but apparently only $AlCl_3$. Thus the compounds $AlCl_3,NOCl$, $AlCl_3,POCl_3$, $AlCl_3,3NH_3$, $AlCl_3,KCl$, $AlCl_3,NaCl$ are known.[35] The compound of aluminium and sodium chlorides, $AlNaCl_4$, is very fusible and much more stable in the air than aluminium chloride itself. It seems to be of the same type as the alums. This compound, $AlNaCl_4$, is employed in the extraction of metallic aluminium, as we shall presently proceed to describe. Aluminium bromide, which is obtained by the direct combination of metallic aluminium with bromine, closely resembles the chloride; it melts at 90°, volatilises at 270°, and its vapour density indicates the formula Al_2Br_6. Aluminium iodide is obtained by heating iodine with finely-divided aluminium in a closed tube; it is so

[35] Here we see an instance in confirmation of what has been said in Note 30. We will cite still another instance confirming the power of alumina to enter into complex combinations. Alumina, moistened with a solution of calcium chloride, gives, when ignited, an anhydrous crystalline substance (tetrahedral), which is soluble in acids, and contains $(Al_2O_3)_6(CaO)_{10}CaCl_2$. Even clay forms a similar stoney substance, which might be of practical use.

Among the most complex compounds of aluminium, *ultramarine*, or *lapis lazuli*, must be mentioned. It occurs in nature near Lake Baikal, in crystals, some colourless and others of various tints—green, blue, and violet. When heated it becomes dull and acquires a very brilliant blue colour. In this form it is used for ornaments (like malachite), and as a brilliant blue pigment. Now ultramarine is prepared artificially in large quantities, and this process forms one of the very important conquests of science; for the blue tint of ultramarine has been the object of many scientific researches, which have culminated in the fabrication of this native substance. The most characteristic fact bearing on ultramarine is that when placed in sulphuric acid it evolves hydrogen sulphide and becomes colourless. It is evident that the blue colour of ultramarine is due to the presence of sulphides. If clay be heated in a furnace with sodium sulphate and charcoal (sodium sulphide is formed) without the access of air, then a white mass is formed, which becomes green when heated in the air, and when treated with water it leaves a colourless substance known as 'white ultramarine.' When ignited in the air it absorbs oxygen and turns blue. The reason of the coloration is ascribed to the presence of metallic sulphides or polysulphides, but it is most probable that silicon sulphide, or its oxysulphide, SiOS, is present. At all events, the sulphides play an important part, but the problem is not yet quite clear. To white ultramarine the formula $Na_8Al_6Si_6O_{24}S$ is ascribed. The green probably contains more sulphur, and the blue a still larger quantity. It is supposed to contain $Na_8Al_6Si_6O_{24}S_3$. It is more probable (according to Guckelberger, 1882) that the composition of the blue varies between $Si_{18}Al_{18}Na_{20}S_6O_{71}$ and $Si_{18}Al_{12}Na_{20}S_6O_{69}$. The latter may be expressed as $(Al_2O_3)_6(SiO_2)_{18}(Na_2O)_{20}S_6O_5$, which would indicate the presence of insufficiently-oxidised sulphur in ultramarine.

easily decomposed by oxygen that its vapour even explodes when mixed with it.[36]

Metallic aluminium was first prepared by Wöhler, who did so much for the early study of organic chemistry and made the first synthesis (of urea, Vol. I. p. 399) of organic substances. Wöhler obtained metallic aluminium as a grey powder in 1822 by the action of potassium on aluminium chloride. He afterwards (in 1854) obtained it as a white compact metal, unoxidisable in the air, and acted on with difficulty by acids. Owing to the vast and wide occurrence of clay, many efforts have been made in investigating in detail the methods for the extraction of this metal. These efforts have been completed (1854) by Sainte-Claire Deville, who is renowned for his doctrine of dissociation. The extraction of this metal requires the preliminary preparation of sodium. Experiments on a large scale have proved that the alloys of aluminium have many valuable properties, whilst the metal itself has not proved to be so suitable for technical purposes as was at first thought. Nitric acid, indeed, does not act on it, but the alkalis, alkaline substances, and even salts—for instance, moist table salt—humidity, &c., tarnish it, and hence objects made of aluminium suffer at the surfaces, alter, and cannot, as was hoped, replace the precious metals, from which it differs in its extreme lightness. Some alloys made with aluminium are, however, very valuable in their properties and applications.

The technical method of the preparation of metallic aluminium is based on the decomposition of the above-mentioned compound of sodium and aluminium chlorides by metallic sodium. The compound is obtained by passing the vapour of aluminium chloride (evolved from an ignited mixture of alumina, extracted from bauxite or cryolite,

[36] At the ordinary temperature aluminium does not decompose water, but if we add to the water a small quantity of iodine, or of hydriodic acid and iodine, or of aluminium iodide and iodine, then hydrogen is abundantly evolved. It is evident that here the reaction proceeds at the expense of the formation of Al_2I_6, and that this substance, with water, gives aluminium hydroxide and hydriodic acid, which, with aluminium, evolves hydrogen. Aluminium probably belongs to the metals having a greater affinity for oxygen than for the halogens (Chapter XI. Note 13).

All these halogen compounds of aluminium are soluble in water. *Aluminium fluoride*, AlF_3 (Al_nF_{3n}), is insoluble in water. It is obtained by dissolving alumina in hydrofluoric acid; a solution is then formed, but it contains an excess of hydrofluoric acid. When this solution is evaporated, crystals containing Al_2F_6,HF,H_2O are obtained. They are also insoluble in water. By saturating the above solution with a large quantity of alumina, and then evaporating, we obtain crystals having the composition $Al_2F_6,7H_2O$. All these compounds, when ignited, leave insoluble anhydrous aluminium fluoride. It forms colourless rhombohedra, which are non-volatile, of sp. gr. 3·1, and are decomposed by steam into alumina and hydrofluoric acid. The acid solution apparently contains a compound which has its corresponding salts; by the addition of a solution of potassium fluoride, a gelatinous precipitate of AlK_3F_6 is obtained. A similar compound occurs in nature—namely, $AlNa_3F_6$, or *cryolite*, sp. gr. 3·0.

with charcoal in a stream of chlorine) over red-hot salt, when, if the temperature be sufficiently high, the compound $AlNaCl_4$ is itself volatilised, and may in this manner be obtained pure. A mixture of this compound with salt and fluor spar, or with cryolite, is heated with a certain excess of sodium, cut into small lumps. On a large scale this operation is carried on in special furnaces with a small access of air and at a high temperature. The decomposition essentially takes place according to the equation $NaAlCl_4 + 3Na = 4NaCl + Al$. Neither charcoal nor zinc will reduce the oxygen compounds of aluminium; even sodium and potassium do not act on alumina.[37]

Aluminium has a white colour resembling that of tin—that is, it is greyer than silver, it has the feebly dull lustre of tin, but compared to tin and pure silver aluminium is very hard. Its density is 2·67—that is, it is nearly four times lighter than silver. It melts at an incipient red heat (600°), and in so doing is so slightly oxidised that it may be easily cast into moulds, and may be obtained in large masses in this manner. At the ordinary temperature it does not alter in the air, and if taken in a compact mass it burns with great difficulty at a white heat; but in thin sheets, into which it may be rolled, or as a very fine wire, it burns with a brilliant white light, because it forms an infusible and non-volatile oxide. Aluminium itself is non-volatile at a furnace heat. Dilute sulphuric acid has no action on it, but the strong acid dissolves it, especially with the aid of heat. Nitric acid, dilute or strong, has no action whatever on it. However, hydrochloric acid dissolves aluminium with great ease, as also do solutions of caustic soda and potash. In the latter cases hydrogen is evolved.

Aluminium forms alloys with different metals with great ease. Among them the copper alloy is of practical use. It is called *aluminium bronze*. This alloy is prepared by immersing 11 p.c. to 12 p.c. by weight of metallic aluminium in molten copper at a white heat. The formation of the alloy is accompanied by the development of a considerable quantity of heat, so that the alloy glows to a bright white heat. This alloy, which corresponds with the composition $AlCu_3$,

[37] Originally the manufacture of aluminium was carried on at Salindres, near Alais, in the South of France. At present it is produced in very large quantities in England. A great number of methods have been tried for the preparation of aluminium and its alloys with copper and iron, from cryolite and clay, especially by the aid of the galvanic current, but as yet the most advantageous method is that given by Deville. There is no doubt that in time the alloys of aluminium will be very widely used, and therefore the manufacture of aluminium will extend; but it is difficult to imagine that the cost of extraction of the metal will decrease sufficiently for it to replace iron, copper, zinc, and other common metals, whose properties are very much altered when alloyed with aluminium (for example, their hardness, casting capacities, &c.).

presents an exceedingly homogeneous mass, especially if perfectly pure copper is taken. It is distinguished for its capacity to fill up the most minute impressions of the mould into which it may be cast, and by its extraordinary elasticity and toughness, so that objects cast from it may be hammered, drawn, &c., and at the same time it is fine-grained and exceedingly hard, takes an excellent polish, and, what is most important, its surface then remains almost unchangeable in the air, and has a colour and lustre which may be compared to that of gold alloys. Hence aluminium bronze is much used in the arts for making spoons, watches, vessels, forks, knives, and for ornaments, &c. No less important is the fact that the admixture of one-thousandth part of aluminium with steel renders its castings homogeneous (free from cavities) to an extent that could not be arrived at by other means, nor does the quality of the steel in any respect lose by this admixture, but rather is it improved. In a pure state, aluminium is only employed for such objects as require the hardness of metals with comparative lightness, such as telescopes and various physical apparatus.

According to the periodic system of the elements, the analogues of magnesium are zinc, cadmium, and mercury in the second group. So also in the third group, to which aluminium belongs, we find its corresponding analogues *gallium*, *indium*, and *thallium*. They are all three so rarely and sparingly met with in nature that they could only be discovered by means of the spectroscope. This fact shows that they are partially volatile, as should be the case according to the property of their nearest neighbours, the very volatile zinc, cadmium, and mercury. Like them, in gallium, indium, and thallium the density of the metal, decomposability of compounds, &c., rises with the atomic weight. But here we find a peculiarity which does not exist in the second group. In the latter, the fusibility increases with the atomic weight of magnesium, zinc, cadmium, and mercury; indeed, the heaviest metal—mercury—is a liquid. In the third group it is not so. In order to understand this it is sufficient to turn our attention to the elements of the further groups of the uneven series—for instance, to the V. group, containing phosphorus, arsenic, and antimony, or to the VI. group, where are sulphur, selenium, and tellurium, and also to the VII. group, where chlorine, bromine, and iodine are situated. In all these instances the fusibility decreases with a rise of atomic weight; the members of the higher series, the elements of a high atomic weight, fuse with greater difficulty than the lighter elements. The representatives of the uneven series of the III. group, aluminium, gallium, indium, thallium, forming, as they do, a transition, present

a, so to say, intermediate phenomenon. Here the most fusible of all is the medium metal gallium,[38] which fuses at the heat of the hand; whilst indium, thallium, and aluminium fuse at much higher temperatures.

Zinc (II. group), which has an atomic weight 65, should be followed in the III. group by an element with an atomic weight of about 69. It will be in the same group as Al, and should consequently give R_2O_2, RCl_3, $R_2(SO_4)_2$, alums, and like compounds analogous to those of aluminium. Its oxide should be more easily reducible to metal than alumina, just as zinc oxide is more easily reduced than magnesia. The oxide R_2O_3 should, like alumina, have feeble but clearly-expressed basic properties. The metal reduced from its compounds should have a greater atomic volume than zinc, because in the fifth series, proceeding from zinc to bromine, the volume increases. And as the volume of zinc = 9·2, and of arsenic = 18, therefore that of our metal should be near to 12. This is also evident from the fact that the volume of aluminium = 11, and of indium = 14, and our metal is situated in the III. group, between aluminium and indium. If its volume = 11·5 and its atomic weight be about 69, then its density will be nearly 5·9. The fact of zinc being more volatile than magnesium gives reason for thinking that the metal in question will be more volatile than aluminium, and therefore for expecting its discovery by the aid of the spectroscope, &c.

These properties were indicated by me for the analogue of aluminium in 1871, and I named it (*see* Chapter XV.) eka-aluminium. In 1875, Lecoq de Boisbaudran, who had done much work in spectrum analysis, discovered a new metal in a zinc blende from the Pyrenees (Pierrefitte). He recognised its individuality and distinction from zinc, cadmium, indium, and the other companions of zinc by means of the spectroscope; but he obtained only several fractions of a centigram of it free. But few of its reactions were determined, as, for instance, that barium carbonate precipitates a new oxide from its salts (alumina, as is known, is also precipitated). Lecoq de Boisbaudran named the newly-discovered metal *gallium*. As one would expect the same properties for eka-aluminium as were observed in gallium, I at the time pointed out this fact in the Memoirs of the Paris Academy of Sciences. All the subsequent observations of Lecoq de Boisbaudran

[38] It is the same in the IV. group of the uneven series, where tin is the most fusible. So the temperature of fusion rises on both sides of tin (silicon is very infusible; germanium, 900°; tin, 230°; lead, 326°); as it also does in the III. group, starting from gallium, for indium fuses at 176°, more difficultly than gallium but more easily than thallium (294°). Aluminium also fuses with greater difficulty than gallium.

confirmed the identity between the properties of gallium and those indicated for eka-aluminium. Immediately after this the ammonium alum of gallium was obtained, but the most weighty proof of all was shown in the fact that the density of gallium was first found to be different (4·7) from that indicated above, whilst afterwards, when the metal was carefully purified from sodium (which was first used as a reducing agent), it proved to be just that (5·9) which would have been looked for in the analogue of aluminium, eka-aluminium or gallium; and, what was very important, the equivalent (23·3) and atomic weight (69·8) determined by the specific heat (0·08) were shown by experiment to be such as would be expected. These facts confirmed the universality and applicability of the periodic system of the elements. It must be remarked that previous to it there was no means of either foretelling the properties or even the existence of undiscovered elements.[39]

Much more light has been thrown on that element of the aluminium group which follows after cadmium (its position in the periodic system is III., 7, that is, it is in the III. group in the 7th series). This is *indium*, In, which also occurs in small quantities in certain zinc ores. It was discovered (1863) by Reich and Richter (and more fully investigated by Winkler) in the Freiberg zinc ores, and was named indium from the fact that it gives to the flame of a gas-burner a blue coloration, owing to the indigo blue spectral lines proper to it. The equivalent (to hydrogen) of indium =37·7, and if it be an analogue of aluminium, and if the composition of its oxide be In_2O_3, then its atomic weight will be $3 \times 37{\cdot}7$=about 113—that is, near to the atomic weight of cadmium, Cd=112, as aluminium is near to magnesium. If the formula of the indium oxide be taken as In_2O_3 (In=113), then all its properties are known, as has been explained in Chapter XV. The specific heat of the metal confirms its atomic weight, In=113. It has been shown to be equal to 0·057 (according to Bunsen) and 0·055 (according to the author's determination), and these numbers correspond

[39] The spectrum of gallium is characterised by a brilliant violet line having a wave length = 417 millionths of a millimetre. The metal is separated from the solution, containing a mixture of the many metals occurring in the zinc blende, on the basis of the following reactions: it is precipitated by sodium carbonate in the first portions; it gives a sulphate which, on boiling, easily decomposes into a basic salt, very slightly soluble in water; and it is deposited in a metallic state from its solutions by the action of a galvanic current. It fuses at +80°, and, when once fused, it remains liquid for some time. It oxidises with difficulty, evolves hydrogen from hydrochloric acid and from potassium hydroxide, and, like all feeble bases (for instance, alumina and indium oxide), it easily forms basic salts. The hydroxide is soluble in a solution of caustic potash, and slightly so (like alumina) in caustic ammonia.

with the atomic weight 113, because the product of 113 into 0·56 is equal to 6·3, the atomic heat of other metals.[40]

Inasmuch as we found among the analogues of magnesium in the II. group a metal, mercury, heavier and more easily reduced than the rest, and giving two grades of oxidation, so we should expect to find a metal among the analogues of aluminium in the III. group which would be heavy, easily reduced, and give two grades of oxidation, and would have an atomic weight greater than 200. Such is *thallium*. It forms compounds of a lower type, TlX, besides the higher unstable type TlX_3, just as mercury gives HgX_2 and HgX. In the form of the thallic oxide, Tl_2O_3, the base is but feebly energetic, as would be expected by analogy with the oxides Al_2O_3, Ga_2O_3, and In_2O_3, whilst in thallous oxide, Tl_2O, the basic properties are sharply defined, as might be expected according to the properties of the type R_2O (Chapter XV.). *Thallium* was discovered in 1861 by Crookes and by Lamy in certain pyrites. When pyrites are employed in the manufacture of sulphuric acid, they are burned, and they give besides sulphurous anhydride the vapours of various substances which accompany the sulphur, and are volatile. Among these substances arsenic and selenium are found, and together with them, thallium. These substances accumulate in a more or less considerable quantity in the tubes through which the vapours formed in the combustion of the pyrites have to pass. The sulphurous anhydride passes on to the further chambers, whilst these substances condense on cooling. When the methods of spectrum analysis were discovered (1860), a great number of substances were subjected to spectroscopic research, and it was observed that those sublimations which are obtained in the combustion of certain pyrites contained an element having a very sharply-defined and characteristic spectrum—namely, in the green portion of the spectra it gave a sharp green band (wave length 535 mil-

[40] The vapour density of indium chloride, $InCl_3$ (Note 31), determined by Nillson and Pettersson, confirms this atomic weight.

Indium is separated from zinc and cadmium, with which it occurs, on the basis of the fact that its hydroxide is insoluble in ammonia, that the solutions of its salts give indium when treated with zinc (hence indium is dissolved after zinc by acids), and that they give a precipitate with hydrogen sulphide even in acid solutions. Metallic indium is grey, has a sp. gr. of 7·42, fuses at 176°, does not oxidise in the air, and, when ignited, it first gives a black suboxide, In_4O_3, then volatilises and gives a brown oxide, In_2O_3, whose salts, InX_3, are also formed by the direct action of acids on the metal, hydrogen being evolved. Caustic alkalis do not act on indium, from which it is evident that it is less capable of forming alkaline compounds than aluminium; however, with potassium and sodium hydroxides, solutions of indium salts give a colourless precipitate of the hydroxide, which is soluble in an excess of the alkali, like the hydroxides of aluminium and zinc. Its salts do not crystallise.

lionth millimetres) which did not correspond with any then known element.[41]

Under the action of a galvanic current solutions of thallium salts deposit the metal in the form of a heavy powder. It is of a grey colour like tin, is soft like sodium, and has a metallic lustre. Its specific gravity is 11·8, it melts at 290°, and volatilises at a high temperature. When heated slightly above its melting point it forms an insoluble (in water) higher oxide, Tl_2O_3, as a dark-coloured powder, which is, however, generally accompanied by the lower oxide Tl_2O, which is also black, but soluble in water and alcohol. This solution has a distinctly alkaline reaction. This *thallous oxide* melts at 300°, and is easily obtained from the hydroxide TlHO by igniting it without access of air (in the presence of air the incandescent thallous oxide partly passes into thallic oxide). *Thallous hydroxide*, TlOH, crystallises with one molecule H_2O in yellow prisms, which are very easily soluble in water. Metallic thallium may be used for its preparation, as the metal in the presence of water attracts oxygen from the air and forms the hydroxide. But metallic thallium does not decompose water, although it gives a hydroxide which is soluble in water.[41b] All the other data for the

[41] Thallium was afterwards found in certain micas and in the rare mineral crookesite, containing lead, silver, thallium, and selenium. Its isolation depends on the fact that in the presence of acids thallium forms thallous compounds, TlX. Among these compounds the chloride and sulphate are only slightly soluble, and give with hydrogen sulphide a black precipitate of the sulphide Tl_2S, which is soluble in an excess of acid but insoluble in ammonium sulphide.

[41b] The best method of preparing thallous hydroxide, TlOH, is by the decomposition of the requisite quantity of baryta by thallous sulphate, which is slightly soluble in water; barium sulphate is then obtained in the precipitate and thallous hydroxide in solution. This solubility of the hydroxide is exceedingly characteristic, and forms one of the most important peculiarities of thallium. These lower (thallous) compounds are of the type TlX, and recall the salts of the alkalis. The salts TlX are colourless, do not give a precipitate with the alkalis or ammonia, but they are precipitated by ammonium carbonate, because thallous carbonate, Tl_2CO_3, is sparingly soluble in water. Platinic chloride gives the same kind of precipitate as it does with the salts of potassium – that is, thallous platinochloride, $PtTl_2Cl_6$. All these facts, together with the isomorphism of the salts TlX with those of potassium, again point out what an important significance the types of compounds have in the determination of the character of a given series of substances. Although thallium has a greater atomic weight and greater density than potassium, and although it has a less atomic volume, nevertheless thallous oxide is analogous to the potassium oxide in many respects, because they both give compounds of the same type, RX. We will further remark that thallous fluoride, TlF, is easily soluble in water as well as thallous silicofluoride, $SiTl_2F_6$, but that thallous cyanide, TlCN, is sparingly soluble in water. This, together with the slight solubility of thallous chloride, TlCl, and sulphate, Tl_2SO_4, indicates an analogy between TlX and the salts of silver, AgX.

As regards the higher oxide or the *thallic oxide*, Tl_2O_3, the thallium is trivalent in it—that is, it forms compounds of the type TlX_3. The hydroxide, TlO(OH), is formed by the action of hydrogen peroxide on thallous oxide, or by the action of ammonia on a solution of thallic chloride, $TlCl_3$. It is obtained as a brown precipitate, insoluble in water but easily soluble in acids, with which it gives thallic salts, TlX_3. Thallic chloride, which

chemical and physical properties of thallium, of its two grades of oxidation and of their corresponding salts, are expressed by the position occupied by this metal in virtue of its atomic weight Tl=204, between mercury Hg=200, and lead Pb=206.

Gallium, indium, and thallium belong to the uneven series, and there should be elements of the even series in the III. group corresponding with calcium, strontium, and barium in the II. group. These elements should in their oxides R_2O_3 present basic characters of a more energetic kind than those shown by alumina, just as calcium, strontium, and barium give more energetic bases than magnesium, zinc, and cadmium. Such are *yttrium* and *ytterbium*, which occur in a rare Swedish mineral called *gadolinite*, and which are therefore termed the gadolinite metals. To these belong also the metal *lanthanum*, which accompanies the two other minerals *cerium* and *didymium* in the mineral *cerite*, and which therefore belong to the cerite metals. They all, and certain of the metals accompanying them, give basic oxides R_2O_3. At first their formula was supposed to be RO, but the application of the periodic system required their being counted as elements of the III. and IV. groups, which was also confirmed by the determination of the specific heats of these metals,[42] and better

is obtained by cautiously heating the metal in a stream of chlorine, forms an easily-fusible white mass, which is soluble in water and able to part with two-thirds of its chlorine when heated. An aqueous solution of this salt yields colourless crystals containing one equivalent of water. It is evident from the above that all the thallic salts can easily be reduced to thallous salts by reducing agents such as sulphurous anhydride, zinc, &c. Besides these salts, thallic sulphate, $Tl_2(SO_4)_3,7H_2O$, thallic nitrate, $Tl(NO_3)_3,4H_2O$, &c., are known. These salts are decomposed by water, like the salts of many feeble basic metals—for example, aluminium.

[42] The specific heat of cerium determined (1870) by me, and afterwards confirmed by Hillebrand, corresponds with that atomic weight of cerium according to which the composition of two oxides should be Ce_2O_3 and CeO_2. Hillebrand also obtained metallic lanthanum and didymium by decomposing their salts by a galvanic current, and he found their specific heats to be near that of cerium and to 0·04, and it is therefore justifiable to ascribe them an atomic weight near to that of cerium, as was done on the basis of the periodic law. Up to 1870 yttrium oxide was also given the formula RO. Having re-determined the equivalent of yttrium oxide (with respect to water), and found it to be 74·6, I considered it necessary to also ascribe to it the composition Y_2O_3, because then it falls into its proper place in the periodic system. If the equivalent of the oxide to water =74·6, then it contains 58·6 of metal per 16 of oxygen, and consequently one part by weight of hydrogen replaces 29·3 of yttrium, and if it be regarded as bivalent (oxide, RO), then it would not, by its atomic weight 58·6, find a place in the second group. But it it be counted as trivalent—that is, if the formula of its oxide be R_2O_3 and salts RX_3—then Y=88, and a position is open for it in the third group in the sixth series after rubidium and strontium. These alterations in the atomic weights of the cerite and gadolinite metals were afterwards accepted by Cleve and other investigators, who now ascribe a formula R_2O_3 to all the newly-discovered oxides of these metals. But still the position in the periodic system of certain elements—for example, of holmium, thulium, samarium, and others—has not yet been determined for want of a sufficient knowledge of their pro-

still by the fact that Nilson and Cleve, in their researches on the gadolinite metals (1879), discovered that they contain a particular and very rare element, *scandium*, which by the magnitude of its atomic weight, Sc=44, and in all its properties, exactly corresponds with the metal (previously foretold on the basis of the periodic system) *ekaboron*, whose properties were determined by taking the cerite and gadolinite metals as forming oxides R_2O_3.[43]

perties and state of purity. The same must be said of *russium*, the new metal which accompanies thorium in monacite, and was discovered in 1889 by Chroustchoff.

[43] So, for example, in 1871, in the *Journal of the Russian Physico-Chemical Society* (p. 45) and in Liebig's *Annalen*, Supt. Band viii. 195, I deduced, on the basis of the periodic law, an atomic weight 44 for ekaboron, and Nilson in 1888 found that of scandium, which is ekaboron, to be Sc=44·03. The periodic law showed that the specific gravity of the ekaboron oxide would be about 8·5, that it would have decided but feeble basic properties, and that it would give colourless salts. And this proved to be the case in the scandium oxide. In describing scandium, Cleve and Nilson acknowledge that the particular interest attached to this element is due to its entire identity with the expected element ekaboron. And this true foretelling of properties could only be arrived at by admitting that alteration of the atomic weights of the cerite and gadolinite metals which was one of the first points of the application of the periodic system of the elements to the store of chemical facts. In my first memoirs, namely in the *Bulletin of the St. Petersburg Academy of Sciences*, vol. viii. (1870), and in Liebig's *Annalen* (*l. c.*, p. 168) and others, I particularly insisted on the necessity of altering the then accepted atomic weights of cerium, lanthanum and didymium. Cleve, Höglund, Hillebrand, and Norton, and more especially Brauner, and others accepted the proposed alteration, confirmed my determination of the specific heat of cerium, and gave fresh proofs in favour of the proposed alterations of the atomic weights. The study of the fluorides was particularly important. Placing cerium in the fourth group, the composition of its highest oxide would then be CeO_2, and its compounds CeX_4, and the lower oxide Ce_2O_3 or CeX_3. Brauner obtained the fluoride CeF_4,H_2O corresponding with the first, and a double crystalline salt, $3KF,2CeF_4,2H_2O$, without any admixture of compound of the lower grade CeX_3, as is generally the case with the majority of salts corresponding with CeX_4. It will be seen from these formulæ and from the tables of the elements, that cerium and didymium do not belong to the third group, which is now being described, but we mention them now for the sake of convenience, as all the cerite and gadolinite metals have much in common. These metals, which are rare in nature, resemble each other in many respects, always accompany each other, are with difficulty isolated from each other, and stand together in the periodic system of the elements; they have acquired a peculiar interest owing to their having been the objects of the study in 1870 of Marignac, Delafontaine, Soret, Lecoq de Boisbaudran, Brauner, Cleve, Nilson, the professors of Upsala, and others.

The cerite and gadolinite metals occur in rare siliceous minerals from Sweden, America, the Urals, and Baikal, such as cerite, gadolinite, and orthite; and in yet rarer minerals formed by titanic, niobic, and tantalic acids, such as euxenite in Norway and America, and samarskite in Norway, the Urals, and America, and in a few rare fluorides and phosphates. The insufficiency of material to work upon, and the difficulty and complexity of the separation of the oxides from each other, are the chief reasons why their composition is so imperfectly known. Cerite is the most accessible of these minerals. Besides silica it contains more than 50 p. c. of the oxides of cerium, lanthanum (from 4 p. c.), and didymium. The decomposition of its powder by sulphuric acid gives sulphates, all of which are soluble in water. The other above-mentioned minerals are also decomposed in the same manner. The solution of sulphates is precipitated with free oxalic acid, which forms salts insoluble in water and dilute acids with all the cerite and gadolinite oxides. The oxides themselves are obtained by igniting the oxalates. When

The brevity of this work and the great rarity of the above-mentioned elements will give me the right to exclude their description, all the more as the principles of the periodic system enable many of their

ignited in the air the cerium passes from its ordinary oxide Ce_2O_3 into the higher oxide CeO_2, which is so feeble a base that its salts are decomposed by water, and it is insoluble in dilute nitric acid. Therefore it is always possible to remove all the cerium oxide by repeated ignitions and solutions in sulphuric acid. The further separation of the metals is mainly based on four methods employed by many investigators.

(*a*) A solution of the mixed salts is treated with an excess of solid potassium sulphate. Double salts, such $Ce_2(SO_4)_3,3K_2SO_4$, are thus formed. The gadolinite metals, namely yttrium, ytterbium, and erbium, then remain in solution—that is, their double salts are soluble in a solution of potassium sulphate, whilst the cerite metals—namely, cerium, lanthanum, and didymium—are precipitated, that is, their double salts are insoluble in a saturated solution of potassium sulphate. This ordinary method of separation, however, appears from the researches of Marignac to be so untrustworthy that a considerable amount of didymium and the other metals remain in the soluble portion, owing to the fact that, although individually insoluble, they are dissolved when mixed together. Thus erbium and terbium occur both in the solution and precipitate. Nevertheless, beryllium, yttrium, erbium, and ytterbium belong to the soluble, and scandium, cerium, lanthanum, didymium, and thorium to the insoluble portion. The insoluble (in a solution of potassium sulphate) salt of scandium, for example, has a composition $Sc_2(SO_4)_3,3K_2SO_4$.

(*b*) The oxides obtained by the ignition of the oxalates are dissolved in nitric acid (the nitrates of the cerite metals easily form double salts with those of the alkali metals, and some—for example, the ammonio-lanthanum salt—crystallise very well; they should be studied and applied to the analytical separation of these metals), the solution is then evaporated to dryness, and the residue fused. All nitrates are destroyed by heat; those salts of aluminium and iron, &c., very easily, the salts of the cerite and gadolinite metals also easily (although not so easily as the above), but in different degrees and sequence; so that by carrying the decomposition from the beginning it is possible to destroy the salt of only one metal without touching the others, or leaving them as soluble basic salts. This method, like the preceding and the two following, must be repeated as many as seventy times, in order to attain an in any way constant product of fixed properties, that one in which the decomposed and undecomposed portions would contain one and the same oxide. This method, due to Berlin and worked out by Bunsen, has given in the hands of Marignac and Nilson the best results, especially for the separation of the gadolinite metals, ytterbium and scandium.

(*c*) A solution of the salts is partially precipitated (fractional precipitation) by ammonia; that is, the solution is mixed with a small quantity of ammonia insufficient for the precipitation of the entire quantity of the bases. Thus, the didymium hydroxide is first precipitated from a mixture of the salts of didymium and lanthanum. A partial separation may be arrived at by repeating the solution of the precipitate and fractional precipitation, but a perfectly pure product is scarcely possible.

(*d*) The formates having different degrees of solubility (lanthanum formate 420 parts of water per one of salt, didymium formate 221, cerium formate 360, yttrium and erbium formates easily soluble) give a possibility of separating certain of the gadolinite metals from each other by a method of fractional solution and precipitation, as Bunsen, Bahr, Cleve, and others pointed out.

The best method of separating these metals is not known, for they are so like each other. There are also only a few *methods of distinguishing* them from each other, and we can only add the following four to the above.

[a] The faculty of oxidising into a higher oxide. This is very characteristic for cerium, which gives the oxides Ce_2O_5 and CeO_2 or Ce_2O_4. Didymium also gives one colourless oxide, Di_2O_3, which is capable of forming salts (of a lilac colour), and another, according to Brauner, Di_2O_5 which is dark brown and does not form salts, as far as is known, and

properties to be foreseen, and as their practical uses (cerium oxalate is used in medicine, and didymium oxide in the manufacture of glass)

which (like ceric oxide) acts as an oxidising agent, like the higher oxides of tellurium, manganese, lead, and others. Lanthanum, yttrium, and many others are not capable of such oxidation. The presence of the higher oxides may be recognised by ignition in a stream of hydrogen; by which means the higher oxides are reduced to the lower, which then remain unaltered.

[b] The majority of the salts of the gadolinite and cerite metals are colourless, but those of didymium and erbium are rose-coloured, the salts of the higher oxide of cerium, CeX_4, yellow, of the higher oxide of terbium, yellow, &c. Thus, the first metals obtained from gadolinite were yttrium, giving colourless, and erbium, giving rose-coloured, salts. Afterwards it was found that the salts of erbium of former investigators contained numerous colourless salts of scandium, ytterbium, &c., so that a coloration sometimes determines the presence of a small impurity, as was long known to be the case in minerals, and therefore this point of distinction cannot be considered trustworthy.

[c] In a solid state and in solutions, the salts of didymium, samarium, holmium, &c., give characteristic absorption spectra, as we pointed in Chap. XIII., and this naturally is connected with the colour of these salts. The most important point is, that those metals which do not give an absorption spectrum—for example, lanthanum, yttrium, scandium, and ytterbium—may be obtained free from didymium, samarium, and the other metals giving absorption spectra, because the presence of the latter may be easily recognised by means of the spectroscope, whilst the presence of the former in the latter cannot be distinguished, and therefore the purification of the former can be carried further than that of the latter. We may further remark that the sensitiveness of the spectrum reaction for didymium is so great that it is possible with a layer of solution half a metre thick to recognise the presence of 1 part of didymium oxide (as salt) in 40000 parts of water. Cossa determined the presence of didymium (together with cerium and lanthanum) in apatites, limestones, bones, and the ashes of plants by this method. The main group of dark lines of didymium correspond with wave lengths of from 580 to 570 millionths mm.; and the secondary to about 520, 730, 480, &c. The chief absorption bands of samarium are 472–486, 417, 500, and 559. Besides which, Crookes applied the investigation of the spectra of the phosphorescent light which is emitted by certain earths in an almost perfect vacuum, when an electric discharge is passed through it, to the discovery and distinction of these rare metals. But it would seem that the smallest admixture of other oxides (for example, bismuth, uranium) so powerfully influences these spectra that the radical distinctions of the oxides cannot be seized by this method. Besides which, the spectra obtained by the passage of sparks through solutions or powders of the salts are determined and applied to distinguishing the elements, but as spectra vary with the temperature and elasticity (concentration) this method cannot be considered as trustworthy.

[d] The most important point of distinction of individual metallic oxides is given by the direct *determination of their equivalent with respect to water*—that is, the amount of the oxide by weight which combines (like water) with 80 parts by weight of sulphuric anhydride, SO_3, for the formation of a normal salt. For this purpose the oxide is weighed and dissolved in nitric acid, sulphuric acid is then added, and the whole is evaporated to dryness over a water-bath and then heated over a naked flame sufficiently strongly to drive off the excess of sulphuric acid, but not sufficiently so to decompose the salt (the salt would then not be perfectly soluble in water); then, knowing the weight of the oxide and of the anhydrous sulphate, we can find the equivalent of the oxide. The following are the most trustworthy figures in this respect: scandium oxide 45·35 (Nilson), yttrium oxide 75·7 (Cleve; according to my determination, 1871—74·6), cerous oxide—that is, the lower form of oxidation of cerium, according to various investigators (Bunsen, Brauner, and others) from 108 to 111, the higher oxide of cerium from 85 to 87, lanthanum oxide, according to Brauner, 108, didymium oxide (in salts of the ordinary lower form of oxidation) about 112 (Marignac, Brauner, Cleve), samarium oxide about 116

are very limited, by reason of their great rarity in nature, and the difficulty of separating them from one another.

(Cleve), ytterbium oxide 131·3 (Nilson). It may not be superfluous to here turn attention to the fact that the equivalent of the oxides of all the gadolinite and cerite metals for water distribute themselves into four groups with a somewhat constant difference of nearly 30. In the first group is scandium oxide with equivalent 45, in the second, yttrium oxide 76, in the third, lanthanum, cerium, didymium, and samarium oxides with equivalent about 110, and, in the fourth, erbium, ytterbium, and thorium oxides with equivalents about 131. The common difference of period is nearly 45. And if we ascribe the type R_2O_3 to all the oxides—that is, if we triple the weight of the equivalent of the oxide—we shall obtain a difference of the groups nearly equal to 90, which, for two atoms of the metal, forms the ordinary periodic difference of 45. If one and the same type of oxide R_2O_3 be ascribed to all these elements (as now generally accepted, there in many cases being insufficiently trustworthy data), then the atomic weights should be Sc = 44, Y = 89, La = 138, Ce = 140, Di = 144, Sm = 150, Yb = 173, also terbium 147, holmium 162, alpha-yttrium 157, erbium 166, thulium 170, decipium 171. But it must be observed that if thorium were counted as giving an oxide R_2O_3, then its atomic weight would be 174, and then there would be no other place in the system of the elements, except that occupied by ytterbium. Besides which, it may be an instance of basic salts. If, for example, an element with an atomic weight 90 gave an oxide RO_2, but salts ROX_2, then by counting its oxide as R_2O_3 its atomic weight would be 159.

All the points distinguishing many gadolinite and cerite elements have not been sufficiently firmly established in certain cases (for example, with decipium, thulium, holmium, and others). At present the most certain are yttrium, scandium, cerium, and lanthanum. In the case of didymium, for example, there is still much that is doubtful. Didymium, discovered, in 1842, by Mosander after lanthanum, differs from the latter in its absorption spectrum and the lilac-rose colour of its salts. Delafontaine (1878) separated samarium from it. Welsbach showed that it contains two particular elements neodymium and praseodymium, and Becquerel (1887), by investigating the spectrum of crystals, recognised the presence of six individual elements. Therefore, probably many of the now recognised elements contain a mixture of various others, and as yet there is not enough confirmation of their individuality. As regards yttrium, scandium, cerium, and lanthanum, which have been established without doubt, I think that, owing to their great rarity in nature and chemical practice, it would be superfluous to describe them further in so elementary a work as the present.

CHAPTER XVIII

SILICON AND THE OTHER ELEMENTS OF THE FOURTH GROUP

CARBON, which gives the compounds CH_4 and CO_2, belongs to the fourth group of elements. The nearest element to carbon is silicon, which forms the compounds SiH_4 and SiO_2; its relation to carbon is like that of aluminium to boron or phosphorus to nitrogen. As carbon composes the principal and most essential part of animal and vegetable substances, so is silicon almost an inevitable component part of the rocky formations of the earth's crust. Silicon hydride, SiH_4, like CH_4, has no acid properties, but silica, SiO_2, shows feeble acid properties like carbonic anhydride. In a free state silicon is also a non-volatile, slightly energetic non-metal, like carbon. Therefore the form and nature of the compounds of carbon and silicon are very similar. In addition to this resemblance, silicon presents one exceedingly important distinction from carbon: namely, the higher degree of oxidation. That is, silica, silicon dioxide, or silicic anhydride, SiO_2, is a solid, non-volatile, and exceedingly infusible substance, very unlike carbonic anhydride, CO_2, which is a gas. This expresses the essential peculiarity of silicon.

The cause of this distinction may be most probably sought for in the polymeric composition of silica compared with carbonic anhydride. The molecule of carbonic anhydride contains CO_2, as seen by the density of this gas; whilst, on the contrary, it can be hardly possible that the density of the vapours of silica, if it were to evaporate, would correspond with the formula SiO_2, it may be imagined that it would correspond to a far higher atomic weight of Si_nO_{2n}, principally from the basis that SiH_4 is also a gas like CH_4, $SiCl_4$ is also a liquid and volatile, boiling at 57°—that is, even lower than CCl_4, which boils at 76°. In general, analogous compounds of silicon and carbon have nearly the same boiling points if they are liquid and volatile.[1] From this it might be expected that silicic

[1] Chloroform, $CHCl_3$, boils at 60°, and silicon chloroform, $SiHCl_3$, at 34°; silicon ethyl, $Si(C_2H_5)_4$, boils at about 150°, and its corresponding carbon compound, $C(C_2H_5)_4$,

anhydride, SiO_2, would be a gas like carbonic anhydride, whilst in reality silica is a hard non-volatile substance, and therefore it may with great certainty be considered that in this condition it is polymeric with SiO_2, as on polymerisation—for instance, when cyanogen passes into paracyanogen, or hydrocyanic acid into cyanuric acid (Chapter IX.)—very frequently gaseous or volatile substances change into solid, non-volatile, and physically denser and more complex substances.[2] On account of this polymerisation of silica, and its diffusion and signification in nature, we will first make acquaintance with free silicon and its volatile compounds, as substances in which the analogy of silicon with carbon is shown, not only in a chemical but also in a physical sense.[3]

at about 120°; ethyl orthosilicate, $Si(OC_2H_5)_4$, boils at 160°, and ethyl orthocarbonate, $C(OC_2H_5)_4$, at 158°; that is, generally speaking, the compounds of silicon, if they are volatile, boil at similar or lower temperatures than the compounds of carbon. Their specific volumes in a liquid state are also nearly equal—that is, those of the silicon compounds generally are slightly greater than those of the carbon compounds (hence they boil at lower temperatures); for example, the volumes of $CCl_4=94$, $SiCl_4=112$, $CHCl_3=81$, $SiHCl_3=82$, of $C(OC_2H_5)_4=186$, and $Si(OC_2H_5)_4=201$. The corresponding salts have also nearly equal specific volumes; for example, $CaCO_3=37$, $CaSiO_3=41$. It is impossible to compare SiO_2 and CO_2, because their physical states are so widely different.

[2] A property of intercombination is observable in the atoms of carbon, and a faculty for intercombination, or polymerisation, is also seen in the unsaturated hydrocarbons and carbon compounds in general. In silicon a property of the same nature is found to be particularly developed in silica, SiO_2, which is not the case with carbonic anhydride. The faculty of the molecules of silica for combining both with other molecules and among themselves is expressed in the formation of most varied compounds with bases, in the formation of hydrates with a gradually decreasing proportion of water down to anhydrous silica, in the colloid nature of the hydrate (the molecules of colloids are always complex), in the formation of polymeric ethereal salts, and in many other points which will be considered in the sequel. Having come to the conclusion as to the polymeric state of silica since the years 1850–1860, I have found it to be confirmed by all subsequent researches on the compounds of silica, and, if I mistake not, this view, partially enunciated by Graham, has now been accepted by many.

As polymerisation is always accompanied by an increase in density, not only in a gaseous but also in a liquid and solid state (for example, the density of benzene, C_6H_6, is less than that of cinnamene, C_8H_8, or ditolyl, $C_{14}H_{14}$), the comparatively high density of silica confirms to a certain extent the view as to its polymerised state. Indeed, a close agreement is observed on comparing the specific volumes of the corresponding compounds of carbon and silicon; for example, the specific volume of chloroform, $CHCl_3$, is about 81 (according to Thorpe), and of silicon chloroform about 82 (Buff and Wöhler), and the volume of carbonic anhydride in a liquid state is about 46, and in a solid form it is naturally less, although not greatly so, whilst the specific volume of silica in an amorphous state (sp. gr. = 2·2) is 27, and in the form of quartz (sp. gr. = 2·65) less than 23.

[3] It was only after Gerhardt, and, in general, subsequently to the establishment of the true atomic weights of the elements (Chapter VII.), that a true idea of the atomic weight of silicon and of the composition of silica was arrived at from the fact that the molecules of $SiCl_4$, SiF_4, $Si(OC_2H_5)_4$, &c., never contain less than 28 parts of silicon.

The question *of the composition of silica* was long the subject of the most contradictory statements in the history of science. In the last century Pott, Bergmann, and Scheele distinguished silica from alumina and lime. In the beginning of the present

Free silicon is obtained in the amorphous and crystalline states. Amorphous silicon is produced, like aluminium, by decomposing the

century Smithson for the first time expressed the opinion that silica was an acid, and the minerals of rocks salts of this acid. Berzelius determined the presence of oxygen in silica—namely, that 8 parts of oxygen were united with 7 of silicon. The composition of silica was first expressed as SiO (and for the sake of shortness S only was sometimes written instead). An investigation in the amount of silica present in crystalline minerals showed that the amount of oxygen in the bases bears a very varied proportion to the amount of oxygen in the silica, and that this ratio varies from 2 : 1 to 1 : 3. The ratio 1 : 1 is also met with, but the majority of these minerals are rare. Other more common minerals contain a larger proportion of silica, the ratio between the oxygen of the bases and the oxygen of the silica being equal to 1 : 2, or about this; such are the augites, labradorites, oligoclase, talc, &c. The higher ratio 1 : 3 is known for a widely-distributed series of natural silicates—for example, the felspars. Those silicates in which the amount of oxygen in the bases is equal to that in the silica are termed *monosilicates*; their general formula will be $(RO)_2SiO_2$ or $(R_2O_3)_2(SiO_2)_3$. Those in which the ratio of the oxygen is equal to 1 : 2 are termed *bisilicates*, and their general formula will be $ROSiO_2$ or $R_2O_3(SiO_2)_3$. Those in which the ratio is 1 : 3 will be *trisilicates*, and their general formula $(RO)_2(SiO_2)_3$ or $(R_2O_3)_2(SiO_2)_9$.

In these formulæ the now established composition of SiO_2—that is, that in which the atom of Si = 28—is employed. Berzelius, who made an accurate analysis of the composition of felspar, and recognised it as a trisilicate formed by the union of potassium oxide and alumina with silica, in just the same manner as the alums are formed by sulphuric acid, gave silica the same formula as sulphuric anhydride—that is, SiO_3. In this case the formula of felspar would be exactly similar to that of the alums—that is, $KAl(SiO_4)_2$, like the alums, $KAl(SO_4)_2$. If the composition of silica be represented as SiO_3, then the atom of silicon must be recognised as equal to 42 (if O = 16; or if O = 8, as it was before taken to be, Si = 21).

The former formulæ of silica, SiO(Si = 14) and SiO_3(Si = 42), were first changed into the present one, SiO_2(Si = 28), on the basis of the following arguments:—An excess of silica occurs in nature, and in siliceous rocks free silica is generally found side by side with the silicates, and one is therefore led to the conclusion that it has formed acid salts. Therefore it would be untrue to consider the trisilicates as normal salts of silica, for they contain the largest proportion of silica; it is much better to admit another formula with a smaller proportion of oxygen for silica, and it then appears that the majority of minerals are normal or slightly basic salts, whilst some of the minerals predominating in nature contain an excess of silica—that is, belong to the order of acid salts.

At the present time, when there is a general method (Chapter VII.) for the determination of atomic weights, the volumes of the volatile compounds of silica show that its atomic weight Si = 28, and then silica is SiO_2. Thus, for example, the vapour density of silicon chloride with respect to air is, as Dumas showed (1862), 5·94, and hence with respect to hydrogen it is 85·5, and consequently its molecular weight will be 171 (instead of 170 as per theory). This weight contains 28 parts of silicon and 142 parts of chlorine, and as an atom of the latter is equal to 35·5, the molecule of silicon chloride contains $SiCl_4$. As two atoms of chlorine are equivalent to one of oxygen, the composition of silica will be SiO_2—that is, the same as stannic oxide, SnO_2, or titanic oxide, TiO_2, and the like, and also as carbonic and sulphurous anhydrides, CO_2 and SO_2. But silica bears but little physical resemblance to the latter compounds, whilst stannic and titannic oxides resemble silica both physically and chemically. They are non-volatile, crystalline, insoluble, are colloids, also form feeble acids like silica, &c., and therefore they might be expected to form analogous compounds, and be isomorphous with silica, as Marignac (1859) found actually to be the case. He obtained stannofluorides, for example—an easily soluble strontium salt, $SrSnF_6,2H_2O$, corresponding with the already long known silicofluorides, such as $SrSiF_6,2H_2O$. Both these salts are perfectly similar in crystalline form

double fluoride of sodium and silicon (sodium silicofluoride) by means of sodium :

$$Na_2SiF_6 + 4Na = 6NaF + Si.$$

By treating the mass thus obtained with water the sodium fluoride may be extracted and the residue will consist of brown, powdery silicon. In order to free it from any silica which might be formed, it is treated with hydrofluoric acid. This silicon powder is not lustrous; when heated it easily ignites, but does not completely burn. It fuses when very strongly heated, and reminds one of carbon. Crystalline silicon is obtained in a similar way, but by substituting an excess of aluminium for the sodium :

$$3Na_2SiF_6 + 4Al = 6NaF + 4AlF_3 + 3Si.$$

The part of the aluminium remaining in the metallic state dissolves the silicon, and the latter separates from the solution on cooling in a crystalline form. The excess of aluminium after the fusion is removed by means of hydrochloric acid and hydrofluoric acid. Silicon obtained by means of aluminium has a laminar crystalline structure. The best silicon crystals are obtained from molten zinc; 15 parts of sodium silicofluoride are mixed with 20 parts of zinc and 4 parts of sodium, and the mixture is thrown into a strongly-heated crucible, a layer of common salt being used to cover it over; when the mass fuses it is stirred, cooled, treated with hydrochloric acid, and then washed with nitric acid. Silicon, especially when crystalline, like graphite and charcoal, does not in any way act on the above-mentioned acids. It forms black, very brilliant, regular octahedra having a specific gravity of 2·49; it is a bad conductor of electricity, and does not burn even in pure oxygen. The only acid which acts on it is a mixture of hydrofluoric and nitric acids; but caustic alkalis dissolve it like aluminium, with evolution of hydrogen, thus showing the acid character of silicon. In general silicon strongly resists the action of reagents, as also do boron and carbon. Crystalline silicon was obtained in 1855 by Deville, and amorphous silicon in 1826 by Berzelius.[4]

(monoclinic; angle of the prism, 83 for the former and 84 for the latter; inclination of the axes, 103° 46′ for the latter and 103° 30′ for the former), as they are also similar in composition—that is, they are isomorphous. We may here add that the specific volume of silica in a solid form is 22·6, and of stannic oxide 21·5.

[4] It is very remarkable that silicon decomposes carbonic anhydride at white heat, forming a white mass which, after being treated with potassium hydroxide and hydrofluoric acid, leaves a very stable yellow substance of the formula SiCO, which is formed according to the equation, $3Si + 2CO_2 = SiO_2 + 2SiCO$. It is also slowly formed when silicon is heated with carbonic oxide. It is not oxidised when heated in oxygen. A mixture of silicon and carbon, when heated in nitrogen, gives the compound Si_2C_2N, which is also very stable.

Silicon hydride, SiH_4, analogous to marsh gas, was obtained first of all in an impure state, mixed with hydrogen, by two methods: by the action of an alloy of silicon and magnesium on hydrochloric acid,[5] and by the action of the galvanic current on dilute sulphuric acid, using electrodes of aluminium, containing silicon. In these cases silicon hydride is set free, together with hydrogen, and the presence of the hydride is shown by the fact that the hydrogen separated ignites spontaneously on coming into contact with the air, forming water and silica. The formation of silicon hydride by the action of hydrochloric acid on magnesium silicide is perfectly akin to the formation of phosphuretted hydrogen by the action of hydrochloric acid on calcium phosphide, to the formation of hydrogen sulphide by the action of acids on many metallic sulphides, and even to the formation of hydrocarbons by the action of hydrochloric acid on white cast iron. On heating silicon hydride—that is, on passing it through an incandes-

On this basis Schützenberger recognises a group, C_2Si_2, as capable of combining with O_2 and N, like C.

[5] This alloy, as Beketoff and Cherikoff showed, is easily obtained by directly heating finely-divided silica (the experiment may be conducted in a test tube) with magnesium powder (Chapter XIV. Notes 17, 18). The substance formed, when thrown into a solution of hydrochloric acid, evolves spontaneously inflammable and impure silicon hydride, so that the self-inflammability of the gas is easily demonstrated by this means.

In 1850–60 Wöhler and Buff obtained an alloy of silicon and magnesium by the action of sodium on a molten mixture of magnesium chloride, sodium silicofluoride, and sodium chloride. The sodium then simultaneously reduces the silicon and magnesium.

Friedel and Ladenburg subsequently prepared silicon hydride in a pure state, and showed that it is not spontaneously inflammable in air, at the ordinary pressure, but that it easily takes fire in air, like the mixture prepared by the above methods, under a lower pressure or when mixed with hydrogen. They prepared the pure compound in the following manner: Wöhler showed that when dry hydrochloric acid gas is passed through a slightly-heated tube containing silicon it forms a very volatile colourless liquid, which fumes strongly in air; this is a mixture of silicon chloride, $SiCl_4$, and *silicon chloroform*, $SiHCl_3$, which corresponds with ordinary chloroform, $CHCl_3$. This mixture is easily separated by distillation, because silicon chloride boils at 57°, and silicon chloroform at 38°. The formation of the latter will be understood from the equation $Si + 3HCl = H_2 + SiHCl_3$. It is an anhydrous inflammable liquid of specific gravity 1·6. It forms a transition product between SiH_4 and $SiCl_4$, and may be obtained from silicon hydride by the action of chlorine, and is itself also transformed into silicon chloride by the action of chlorine. It is also formed from silicon hydride by the action of antimonic chloride. Friedel and Ladenburg, by acting on anhydrous alcohol with silicon chloroform, obtained an ethereal compound having the composition $SiH(OC_2H_5)_3$. This ether boils at 136°, and when acted on with sodium disengages silicon hydride, and is converted into ethyl orthosilicate, $Si(OC_2H_5)_4$, according to the equation $4SiH(OC_2H_5)_3 = SiH_4 + 3Si(OCl_2H_5)_4$ (the sodium seems to be without action), which is exactly similar to the decomposition of the lower oxides of phosphorus, with the evolution of phosphuretted hydrogen. If we designate the group C_2H_5, contained in the silicon ethers by Et, the parallel is found to exact:

$$4PHO(OH)_2 = PH_3 + 3PO(OH)_3;\ 4SiH(OEt)_3 = SiH_4 + 3Si(OEt)_4.$$

Warren (1888) obtained silicon and its alloy with magnesium by heating magnesium in a current of silicon fluoride.

cent tube, it is decomposed into silicon and hydrogen, just like the hydrocarbons, but the caustic alkalis, although without action on the latter, react with silicon hydride according to the equation :

$$SiH_4 + 2KHO + H_2O = SiK_2O_3 + 4H_2.$$

Silicon chloride, $SiCl_4$, is obtained from amorphous anhydrous silica (made by igniting the hydrate) mixed with charcoal,[6] heated to a white heat in a stream of dry chlorine—that is, by that general method by which many other chloranhydrides of acid properties are obtained. Silicon chloride is purified from free chlorine by distillation over metallic mercury. Free silicon forms the same substance when treated with dry chlorine. It is a volatile colourless liquid, which boils at 57° and has a specific gravity of 1·52. It fumes strongly in air, has a pungent smell, and in general has the characteristic properties of the acid chloranhydrides. It is completely decomposed by water, forming hydrochloric acid and silicic acid, according to the equation :

$$SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl.$$[7]

[6] The amorphous silica is mixed with starch, dried, and then charred by heating the mixture in a closed crucible. A very intimate mixture of silica and charcoal is thus formed. In Chapter XI. Note 13, we saw that elements like silicon disengage more heat with oxygen than with chlorine, and therefore their oxygen compounds cannot be directly decomposed by chlorine, but that this can be effected when the affinity of carbon for oxygen is utilised to aid the action.

[7] Silicon chloride shows a similar behaviour with alcohol. This is accompanied by a very characteristic phenomenon; on pouring silicon chloride into anhydrous alcohol a momentary evolution of heat is observed, owing to a reaction of double decomposition, but this is immediately followed by a powerful cooling effect, due to the disengagement of a large amount of hydrochloric acid—that is, there is an absorption of heat from the formation of gaseous hydrochloric acid. This is a very instructive example in this respect; here two simultaneously-accomplished processes—one chemical and the other physical—are divided from each other by time, the latter process evincing itself by a clear fall of temperature. In the majority of cases the two processes proceed simultaneously, and we *only* realise the difference between the heat developed and absorbed. In acting on alcohol, silicon chloride forms ethyl orthosilicate, $SiCl_4 + 4HOC_2H_5 = 4HCl + Si(OC_2H_5)_4$. This substance boils at 160°, and has a specific gravity 0·94. Another salt, ethyl metasilicate, $SiO(OC_2H_5)_2$, is also formed by the action of silicon chloride on anhydrous alcohol; it volatilises above 300°, having a sp. gr. 1·08. This is exceedingly important in this respect, that this ethereal salt is also volatile, and also corresponds with silica, SiO_2: the first ether corresponds to the hydrate $Si(OH)_4$, orthosilicic acid, and the second to the hydrate $SiO(OH)_2$, metasilicic acid. As the nature of hydrates may be judged from the composition of salts, so also, and with perfect right, can ethereal salts serve the same purpose. The composition of an ethereal salt corresponds with that of an acid in which the hydrogen is replaced by a hydrocarbon radicle—for instance, by C_2H_5—and therefore the composition of a hydrate may be realised by replacing this radicle by hydrogen. And, therefore, it may be justly said that there exist at least the two above-mentioned silicic acids. We shall afterwards see that there are really several such hydrates, and that these ethereal salts actually correspond with hydrates of silica is clearly shown from the fact that these ethers are decomposed by water, and that in

The most remarkable of the haloid compounds of silicon is *silicon fluoride*, SiF_4, because it is a gaseous substance only liquefied by intense cold, $-100°$, and on account of its being obtained (Chapter XI.) directly by the action of hydrofluoric acid on silica and its compounds ($SiO_2+4HF=2H_2O+SiF_4$), and is even formed by heating fluorspar with silica ($2CaF_2+3SiO_2=2CaSiO_3+SiF_4$).[8] In order to prepare silicon fluoride, sand or broken glass is mixed with an equal quantity by weight of fluorspar and 6 parts by weight of strong sulphuric acid, and the mixture is gently heated. It fumes strongly in air, reacting with the aqueous vapours, although it is produced from silica and hydrofluoric acid with the separation of water. It is evident that a reverse reaction occurs here; that is to say, the water reacts with the silicon fluoride, but the reaction is not complete. This phenomenon is effected in a similar way to that which occurs when water decomposes aluminium chloride, but at the same time hydrochloric acid dissolves aluminium hydroxide and forms the same aluminium chloride. The relative amount of water present (together with the temperature) determines the limit and direction of the reaction. The faculty which silicon fluoride has of reacting with water is so great that it takes up the elements of water from many substances—for instance, like sulphuric acid, it chars paper. Water dissolves about 300 volumes of this gas, but in this case it is not a common solution which takes place, but a reaction; especially is this the case with a small quantity of silicon fluoride, that is, with an excess of water. During the first absorption of silicon fluoride by water, silicic acid is separated in the form of a jelly, but a certain quantity of the silicon fluoride also remains in liquid, because the hydrofluoric acid formed

moist air they give alcohol and the corresponding hydrate, although the hydrate which is obtained in the residue always corresponds with the second ethereal salt only—that is, it has the composition $SiO(OH)_2$; this form corresponds also to carbonic acid in its ordinary salts. This hydrate is formed as a vitreous mass when the ethyl silicates are kept in air, owing to the action of the atmospheric moisture on them. Its specific gravity is 1·77.

Silicon bromide, $SiBr_4$, as well as silicon bromoform, $SiHBr_3$, are substances closely resembling the chlorine compounds in their reactions, and are obtained in the same manner. Silicon iodoform, $SiHI_3$, boils at about 220°, has a specific gravity of 3·4; reacts in the same manner as silicon chloroform, and is formed, together with silicon iodide, SiI_4, by the action of a mixture of hydrogen and hydriodic acid on heated silicon. Silicon iodide is a solid at the ordinary temperature, fusing at about 120°; it may be distilled in a stream of carbonic anhydride, but easily takes fire in air, and behaves with water and other reagents just like silicon chloride. It may be obtained by the direct action of the vapour of iodine on heated silicon.

[8] This property of calcium fluoride of converting silica into a gas and a vitreous fusible slag of calcium silicate is frequently taken advantage of in the laboratory and in practice in order to remove silica. The same reaction is employed for preparing silicon fluoride on a large scale in the manufacture of hydrofluosilicic acid (see sequel).

dissolves the other part of the silica[9] and forms the so-called *hydrofluosilicic acid*: $H_2SiF_6 = SiF_4 + 2HF = SiH_2O_3 + 6HF - 3H_2O$. That is to say, a metasilicic acid, SiH_2O_3, in which O_3 is replaced by F_6. This view of the composition of hydrofluosilicic acid may be admitted, because it forms a whole series of highly crystallisable and well-defined salts. In general, the whole reaction of water on silicon fluoride may be expressed by the equation: $3SiF_4 + 3H_2O = SiO(OH)_2 + 2SiH_2F_6$. Hydrofluosilicic acid and silicic acid resemble each other as much, and differ as much, in their chemical character as water and hydrofluoric acid. For this reason silicic acid is a feebler acid than hydrofluosilicic acid, and in addition to this the former is insoluble, and the latter soluble, in water.[10]

Hydrofluosilicic acid is also formed if silicic acid is dissolved in a solution of hydrofluoric acid. It is incapable of volatilising without decomposition, and on heating the concentrated acid silicon fluoride is evolved, leaving an aqueous solution of hydrofluoric acid. This is the reason why solutions of hydrofluosilicic acid corrode glass. This decomposition may be further accelerated by the addition of sulphuric

[9] The amount of heat developed by the solution of silicic acid, SiO_2nH_2O, in aqueous hydrofluoric acid, $xHFnH_2O$, increases with the magnitude of x and normally equals $x5600$ heat units, where x varies between 1 and 8. However, when $x = 10$ the maximum amount of heat is developed (= 49500 units), and beyond that the amount decreases (Thomsen).

[10] In reality, however, the reaction would seem to be still more complex, because the aqueous solution of silicon fluoride does not yield a hydrate of silica, but a fluohydrate (Schiff), $Si_2O_3(OH)F$, corresponding to the (pyro) hydrate $Si_2O_3(OH)_2$, equal to $SiO(OH)_2SiO_2$, so that the reaction of silicon fluoride on water is expressed by the equation: $5SiF_4 + 4H_2O = 3SiH_2F_6 + Si_2O_3(OH)F + HF$. However, Berzelius states that the hydrate, when well washed with water, contains no fluorine, which is probably due to the fact that an excess of water decomposes $Si_2O_3(OH)F$, forming hydrofluoric acid and the compound $Si_2O_3(OH)_2$. Water saturated with silicon fluoride disengages silicon fluoride and hydrofluoric acid when treated with hydrochloric acid, therefore the gelatinous precipitate is then dissolved. It may be further remarked that hydrofluosilicic acid has been frequently regarded as $SiO_2,6HF$, because it is formed by the solution of silica in hydrofluoric acid, but only two of these six hydrogens are replaced by metals. On concentration, the solutions of the acid already decompose when they reach a strength of $6H_2O$ per H_2SiF_6, and therefore the acid may be regarded as $Si(OH)_4,2H_2O,6HF$, but the corresponding salts contain less water, and there are even anhydrous salts R_2SiF_6, so that the acid itself is most simply represented as H_2SiF_6.

If gaseous silicon fluoride be passed directly into water, the gas-conducting tube becomes clogged with the precipitated silicic acid. This is best prevented by immersing the end of the tube under mercury, and then pouring the water over the mercury; the silicon fluoride then passes through the mercury, and only comes into contact with the water at its surface, and consequently the gas-conducting tube remains unobstructed. The silicic acid thus obtained soon settles, and a colourless solution with a pleasant but distinctly acid taste is procured.

Mackintosh, by taking 9 p.c. of hydrofluoric acid, observed that in the course of an hour its action on opal attained 77 p.c. of the possible, and did not exceed 1½ p.c. of its possible action on quartz during the same time. This shows the difference of the structure of these two modifications of silica, which will be more fully described in the sequel.

acid, or even of other acids. Hydrofluosilicic acid, when acting on potassium and barium salts, gives precipitates, because the salts of these metals are but sparingly soluble in water: thus

$$2KX + H_2SiF_6 = 2HX + K_2SiF_6.$$

The salt is obtained in the form of very fine octahedra, but the precipitate does not form quickly, and at first appears as a jelly. Nevertheless, the decomposition is complete, and it is taken advantage of for obtaining their corresponding acids from salts of potassium. The sodium salt is far more soluble in water, and crystallises in the hexagonal system. The magnesium salt, $MgSiF_6$, and calcium salt are soluble in water. The salts of hydrofluosilicic acid may be obtained not only by the action of the acid on bases or by double decompositions, but also by the action of hydrofluoric acid on metallic silicates. Sulphuric acid decomposes them, with evolution of hydrofluoric acid and silicon fluoride, and the salts when heated evolve silicon fluoride, leaving a residue of metallic fluoride, R_2F_2.

According to the principle of substitution (Vol. I. p. 256), if silicon forms SiH_4, then a series of hydrates, or hydroxyl derivatives, ought to exist corresponding to it. The first hydrate of an alcoholic character ought to have the composition $SiH_3(OH)$; the second hydrate, $SiH_2(OH)_2$; the third, $SiH(OH)_3$;[11] and the last, $Si(OH)_4$. The last is a hydrate

[11] This circumstance is very important in explaining the nature of the lower hydrates which are known for silicon. If we suppose water to be taken up from the first hydrates (just as formic acid is $CH(OH)_3$ *minus* water), we shall obtain the various lower hydrates corresponding with silicon hydride. When ignited they should, as phosphorous and hypophosphorous acids, disengage silicon hydride and leave a residue of silica behind—*i.e.*, of the oxide corresponding to the highest hydrate—just as organic hydrates (for example, formic acid with an alkali) form carbonic anhydride as the highest oxygen compound. Such imperfect hydrates of silicon, or, more correctly speaking, of silicon hydride, were first obtained by Wöhler (1863) and studied by Geuther (1865), and were named after their characteristic colours.

Leucone is a white hydrate of the composition $SiH(OH)_3$. It is obtained by slowly passing the vapour of silicon chloroform into cold water: $SiHCl_3 + 3H_2O = SiH(OH)_3 + 3HCl$. But this hydrate, like the corresponding hydrate of phosphorus or carbon, does not remain in this state of hydration, but loses a portion of its water. The carbon hydrate of this nature, $CH(OH)_3$, loses water and forms formic acid, $CHO(OH)$; but the silicon hydrate loses a still greater proportion of water, $2SiH(OH)_3$, parting with $3H_2O$, and consequently leaving $Si_2H_2O_3$. This substance must be an anhydride; all the hydrogen previously in the form of hydroxyl has been disengaged, two remaining hydrogens being left from SiH_4. The other similar hydrate is also white, and has the composition Si_3H_2O (nearly). It may be regarded as the above white hydrate $+ SiO_2$. A yellow hydrate, known as *chryseone* (*silicone*), is obtained by the action of hydrochloric acid on an alloy of silicon and calcium; its composition is nearly $Si_6H_4O_5$. Most probably, however, chryseone has a more complex composition, and stands in the same relation to the hydrate $SiH_2(OH)_3$ as leucone does to the hydrate $SiH(OH)_3$, because this very simply expresses the transition of the first compound into the second with the loss of water,

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of silica, because it is equal to $SiO_2 + 2H_2O$; and it is formed by the action of water on silicon chloride, when all four atoms of chlorine are replaced by four hydroxyl groups. It does not, however, remain in this state, but easily loses part of its water.

Silica or silicic anhydride, both in the free state and in combination with other oxides, enters into the composition of most of the rocky formations of the earth's crust. These siliceous compounds are substances varying so much in their properties, crystalline forms, and relations to one another that they are comprised in a special branch of natural science (like the carbon compounds), and are treated of in works on mineralogy; so that, in dealing with them further, we shall only give a short description of these various compounds. It is, first of all, necessary to turn to the description of silica itself, especially as it is not unfrequently met with in nature in a separate state, and often forms whole masses of rocky formations, called 'quartz.' In an anhydrous condition silica appears in the greatest variety of natural forms—sometimes in well-formed crystals, hexagonal prisms, terminated by hexagonal pyramids; sometimes the prism is wanting, and it appears as hexagonal pyramids. If the crystals are colourless and transparent, they are called *rock crystal*. This is the purest form of silica. Prismatic crystals of rock crystal sometimes attain considerable size, and as they are remarkable for their unchangeability, great hardness, and considerable index of refraction, they are used for ornaments, for seals, making necklaces, &c.[12] Rock crystal, coloured with organic matter, in

$SiH_2(OH)_3 - H_2 + H_2O = SiH(OH)_3$. When these lower hydrates are ignited without the access of air, they are decomposed into hydrogen, silicon, and silica—that is, it may be supposed that they form silicon hydride (which decomposes into silicon and hydrogen) and silica (just as phosphorous and hypophosphorous acids give phosphoric acid and phosphuretted hydrogen). When ignited in air, they burn, forming silica. They are none of them acted on by acids, but when treated with alkalis they evolve hydrogen and give silicates; for example, leucone: $SiH_2O_3 + 4KHO = 2SiK_2O_3 + H_2O + 2H_2$. They have no acid properties. Thus, as yet we have no lower acid hydrates of silicon, corresponding, for example, to formic acid, which would give salts when acted on by alkalis. It must not, however, be forgotten that formic acid, when heated with an alkali, gives a carbonate and hydrogen, $CH_2O_2 + 2KHO = CK_2O_3 + H_2O + H_2$. Consequently, a similar decomposition is accomplished with leucone as with formic acid, only at the ordinary temperature.

[12] Two modifications of rock crystal are known. They are very easily distinguished from each other by their relation to polarised light; one rotates the plane of polarisation to the right and the other to the left—in the one the hemihedral faces are right and in the other they are left; this opposite rotatory power is taken advantage of in the construction of polarisers. But, with this physical difference—which is naturally dependent on a certain difference in the distribution of the molecules—there is not only no observable difference in the chemical properties, but not even in the density of the mass. Perfectly pure rock crystal is a substance which is most invariable with respect to its specific gravity. The numerous and accurate determinations made by Steinheil on the specific gravity of rock crystal show that (if the crystal be free from flaws) it is very constant.

contact with which it is sometimes produced in aqueous formations, has a brown or greyish colour, and then bears the name of *cairngorm* or *smoky quartz*. In this form it has the same uses as rock crystal, especially as it is often found in large masses. The same mineral, coloured red or pink by means of manganese or iron oxides, often occurs, especially in aqueous formations, and is often called *amethyst*. When finely-coloured the amethyst is used as a precious stone, but amethysts are not met with in pure crystals of such considerable size as rock crystal. They most frequently occur as small crystals in the cavities formed in other rocky formations, and especially in those formed in silica itself. A similar anhydrous silica is often found in transparent non-crystalline masses, having the same specific gravity as rock crystal itself (2·66). In this case it is called *quartz*. Sometimes it forms complete rocky formations, but more often penetrates or diffuses itself through other rocky formations, together with other siliceous compounds. Thus, in granite, quartz is mixed with felspar and similar substances. Sometimes the colouring of quartz is so considerable that it is hardly transparent in thin sheets, but it is often found in transparent masses slightly coloured with various tints. The resistance of quartz to the action of water is proved in nature on an enormous scale. When water destroys rocky formations, the siliceous minerals which they contain are partly dissolved and partly transformed into clay, &c. But the quartz remains untouched, and in the form of grains in which it existed in the rocky formation; sometimes, when crushed, it is carried away by the water and deposited as sand. Most frequently, the principal part of *sand* consists of quartz grains washed by water from the rocks which it destroys. Naturally, sometimes other rocky substances which are not changed by water, or only slightly acted on by it, are found in sand; but as these latter are more or less changed by the continuous action of water, it is not unusual to find sand which consists almost entirely of pure quartz. Common sand is generally coloured yellow or reddish-brown by foreign mineral matter, consisting principally of ferruginous minerals and clays. The purest, or so-called quartz, sand is, however, rarely found, and is recognised by the absence of colour, and also by the test that when shaken in water

It is equal to 2·66. The unchangeability of rock crystal under the action of reagents, its small hygroscopic capacity, and very great hardness render it a valuable material for certain apparatus of great accuracy; for example, in the construction of normal weights—that is, of weights for exceedingly accurate weighings. The density of rock crystal is constant, and therefore the correction for weighing with these weights in air can be made with perfect confidence in its accuracy, and their unchangeableness under friction and atmospheric action render these weights (naturally, if they are submitted to an accurate comparison between each other) much more exact than any metallic ones.

it does not form any turbidity: this shows the absence of clay; when fused with bases it forms a colourless glass, and on this account is a valuable material for the manufacture of glass. Sands were formed at all periods of the earth's existence; the ancient ones, compressed by strata of more recent formation and permeated with various substances (deposited from the infiltrating water), are sometimes solidified into rock, called *sandstone*, composing, in some places, whole mountain chains, and serviceable as a most excellent building material, on account of the slight change it undergoes under the influence of atmospheric agencies, and on account of the facility with which it may be wrought from rocky formations into immense regularly-shaped flags—the latter property is due to the primary laminar structure of the sand formations deposited, as above-mentioned, by water.

Completely pure anhydrous silica is not only extracted in the condition of rock crystal and quartz having a specific gravity of 2·6, but also in another special form, having other chemical and physical properties. This variety of silica has a specific gravity of 2·2, and is formed by fusing rock crystal or heating silicic acid.[13] Silicic acid, when heated to a dull red heat, completely parts with the contained water, and leaves an exceedingly fine amorphous mass of silica (easily levigated, but difficult to moisten); it is characterised by such excessive friability that, when lightly blown on, a large mass of it rises into the air like a cloud of dust. A mass of anhydrous silica may be poured in this way from one vessel to another like a liquid, like which it takes a horizontal position in the containing vessel. Anhydrous silica, like quartz, does not fuse in the heat of a furnace, but it fuses in the oxy-hydrogen flame into a colourless glassy mass exactly similar to that formed in the same way from rock crystal. In this condition silica has a specific gravity of 2·2. Both forms of silica are insoluble in ordinary acids, and, when they are taken in the state of powder, alkalis in solution act very slowly and feebly on them; in addition to which rock crystal offers much greater resistance to the action of alkalis than the powder obtained by heating the hydrate. The latter, although but slowly, is quite soluble in hot alkaline solutions. This last property appertains in a greater degree to anhydrous silica having a specific gravity of 2·2 than to that which has a specific gravity of 2·6. Hydrofluoric acid more easily transforms the former into silicon fluoride than it does the latter. Both varieties of silica, when taken in the form of

[13] Several other modifications are known as minute crystals. For example, there is a particular mineral first found in Styria and known as *tridymite*. Its specific gravity 2·3 and form of crystals clearly distinguish it from rock crystal; its hardness is the same as that of quartz—that is, slightly below that of the ruby and diamond.

powder, easily combine with bases, forming, on being fused with an alkali, a vitreous slag, which is a salt corresponding with silica. Glass is a similar salt, formed of alkalis and alkaline earthy bases; if the glass does not contain any of the latter—that is, if only alkaline glass be taken—a mass soluble in water is obtained. In order to obtain such *soluble glass*, potassium or sodium carbonates, or, better, a mixture of the two (a more fusible mixture), is fused with fine sand. A still better and further saturation of the alkalis with silica is effected by the action of alkaline solutions on the silicon hydrate met with in nature; for instance, an alkaline solution is often made use of to act on the so-called *tripoli*, or collection of siliceous skeletons of the lowest microscopical infusoria, which is sometimes found in considerable layers in the form of a sandy mass. Tripoli is used for polishing, not only on account of the considerable hardness of the silica, but also because the microscopic bodies of the infusoria have a pointed shape, which, however, is not angular, so that they do not scratch metals like sand.[14] In a boiler, under a certain amount of pressure, tripoli may be dissolved in a solution of caustic soda (or potash), because it contains silica in the shape of hydrate of a specific gravity 2·2, with a slight amount of water. The alkaline solutions of silica obtained by these means contain various relative amounts of silica and alkali. In order to contain the greatest amount of silica, the solution ought to be heated and silicic acid added to it; in order to obtain this hydrate, it is only necessary to take any kind of solution containing silica and alkali, and to add to it, by degrees, some acid—for instance, sulphuric

[14] Silica also occurs in nature in two modifications. The opal and tripoli (infusorial earth) have a specific gravity of about 2·2, and are comparatively easily dissolved in alkalis and hydrofluoric acid. Chalcedony and flint (tinted quartzose concretions of aqueous origin), agate and similar forms of silica of undubitably aqueous origin, and even still containing a certain amount of water, have a specific gravity of 2·6, and correspond with quartz in the difficulty with which they dissolve. This form of silica sometimes permeates the cellulose of wood, forming one of the ordinary kinds of petrified wood. The silica may be extracted from it by the action of hydrofluoric acid, and the cellulose remains behind, which clearly shows that silica in a soluble form (see sequel) has permeated into the cells, where it has deposited the hydrate, which has lost water, and given a silica of sp. gr. 2·6. The quartzose stalactites found in certain caves are also evidently of a like aqueous origin; however, their sp. gr. is 2·6. As crystals of amethyst are frequently found among chalcedonies, and as Friedau and Sarrau (1879) obtained crystals of rock crystal by heating soluble glass with an excess of hydrate of silica in a closed vessel, there is no doubt but that rock crystal itself is formed in the wet way from the gelatinous hydrate. Chroustchoff obtained it directly from soluble silica. Thus this hydrate is able to form both the variety having the specific gravity 2·2 and the more stable variety of sp. gr. 2·6; and they both exist with a small proportion of water and in a perfectly anhydrous state in an amorphous and crystalline form. All these facts are expressed by recognising silica as dimorphous, and their cause must be looked for in a difference in the degree of polymerisation.

or hydrochloric ; then, if the experiment be carried on carefully and the solution be concentrated, the whole mass thickens to a jelly, due to the gelatinous form of the *silicic acid* separated from the salt by the action of the acid. The decomposition may be expressed by the following equation: $Si(ONa)_4 + 4HCl = 4NaCl + Si(OH)_4$. The hydrate separated, $Si(OH)_4$, easily loses part of the water, and forms a jelly, the whole mass gelatinising if the solution be strong enough.[15]

Neither of the two varieties of anhydrous silica, nor the various

[15] The equation given above does not express the actual reaction, for in the first place silica has the faculty for forming compounds with bases developed to the highest degree, even to a greater degree than molybdic and tungstic anhydrides, and therefore the formula $SiNa_4O_4$ is not rightly deduced, if one may so express oneself. And, in the second place, silica gives several hydrates. In consequence of this, the solution does not usually contain $Si(ONa)_4$, but various other grades of combination of silica with bases; and, moreover, the hydrate precipitated does not actually contain so high a proportion of water as $Si(OH)_4$, but always less. The insoluble gelatinous hydrate which separates out is able (before, but not after having been dried) to dissolve in a solution of sodium carbonate. When dried in air its composition corresponds with the ordinary salts of carbonic acid—that is, SiH_2O_3, or $SiO(OH)_2$. If gradually heated it loses water by degrees, and, in so doing, gives various degrees of combination with it. The existence of these degrees of hydration, having the composition $SiH_2O_3nSiO_2$, or, in general, $nSiO_2mH_2O$, where $m<n$, must be recognised, because most varied degrees of combination of silica with bases are known. We shall find a similar phenomenon in molybdic and tungstic acids, so that it is not exceptional. The hydrate of silica, when not dried above 30°, has a composition of nearly $H_4Si_3O_8 = (H_2SiO_3)_2SiO_2$, but at 60° contains a greater proportion of silica—that is, it loses still more water; and at 100° a hydrate of the composition $SiH_2O_32SiO_2$, and at 250° a hydrate having approximately a composition $SiH_2O_37SiO_2$ is obtained. If the water be regarded as a base—that is, as the water of constitution of the hydrate—then the first hydrate, SiO_2,H_2O, will be a monosilicate (silicic acid) corresponding with a series of silicates of the composition $(RO),SiO_2$, whilst the hydrate which is obtained at 100° will correspond with the trisilicates $RO,3SiO_2$.

Hager (1888) obtained a crystalline hydrate, $H_2SiO_3,3H_2O$, by the action of hydrochloric acid on calcium metasilicate, $CaSiO_3$.

These data and the preceding notes show the complexity of the molecules of anhydrous silica. The hydrate, $Si(OH)_4$ (orthosilicic acid), is very unstable, and easily gives metasilicic acid, $SiO(OH)_2$, and the latter also loses a further amount of water with facility and gives the hydrates $(SiO_2)_n(H_2O)_m$, where m becomes less and less than n. In the natural hydrates, this decrement of water proceeds quite consecutively, and, so to say, imperceptibly, until n becomes incomparably greater than m, and when the ratio becomes very large, anhydrous silica of the two modifications 2·6 and 2·2 is obtained. The composition $(SiO_2)_{10},H_2O$ still corresponds with 2·9 p.c. of water, and natural hydrates often contain still less water than this. Thus some opals are known which contain only 1 p.c. of water, whilst others contain 7 and even 10 p.c. As the artificially prepared gelatinous hydrate of silica when dried has many of the properties of native opals, and as this hydrate always loses water easily and consecutively, there can be no doubt that the transition of $(SiO_2)_n(H_2O_m)$ into anhydrous silica, both amorphous and crystalline (in nature, chalcedony), is accomplished gradually. This can only be the case if the magnitude of n be considerable, and therefore the molecule of silica in the hydrate is undoubtedly complex, and, therefore, the anhydrous silica of sp. gr. 2·2 and 2·6 does not contain SiO_2, but a complex molecule, Si_nO_{2n}—that is, the structure of silica is polymeric and complex, and not simple, as represented by the formula SiO_2.

natural gelatinous hydrates, are directly soluble in water. There is, however, a known condition of silica which is soluble in water, *soluble silica*; and silica is found in this state in nature. Small quantities of soluble silica are met with in all waters. Certain mineral springs, and especially hot springs—of which the best known are the Geysers of Iceland and in the North American National Park (Yellowstone Valley)—contain a considerable amount of silica in solution. Such water, permeating the objects it meets with—for instance, *wood*—penetrates into them and deposits silica inside them, that is, transforms them into a petrified condition. Siliceous stalactites, and also many (if not all) forms of silica, are formed by such water. Their formation is founded on the fact that aqueous solutions of silica, under many conditions, separate gelatinous silica; and the latter parts with water and turns into a stony mass. The absorption of silica by plants by means of their roots, and also by the lower organisms having siliceous bodies, is due also to their nourishing themselves with the solutions containing silica continually formed in nature. Thus, in plants, in the straws of the grasses, in hard shave-grass, and especially in the knots of bamboo and other straw-like plants, a considerable quantity of silica is deposited, which must previously have been absorbed by the plants.

Silicic acid is a colloid. The gelatinous silicon hydrate is its hydrogel, the soluble hydrate is the hydrosol (Chapter XVII.). Both varieties may easily be obtained from the alkaline silicates and water-glass. The very same substances—that is, aqueous solutions of soluble glass and acid—taken in the same proportion, may produce either the gelatinous or the soluble silica, according to the way these solutions are mixed together. If the acid be added little by little to the *alkaline silicate*, with continuous stirring, a moment arrives when the whole mass thickens to a jelly, hydrogel; in this case the silicic acid is formed in the midst of the alkaline solution and becomes insoluble. But if the mixing be done in the reverse order—that is, if the soluble glass be added to the acid, or if a quantity of acid be rapidly poured into the solution of the salt—then the separation of the silica takes place in the midst of the acid liquid, and it is obtained in the form of the soluble hydrate, the hydrosol.[16]

[16] The presence of an excess of acid aids the retention of the silica in the solution, because the gelatinous silica obtained in the above manner, but not heated to 60°—that is, containing more water than the hydrate H_2SiO_3—is more soluble in water containing acid than in pure water. This would seem to indicate a feeble tendency of silica to combine with acids, and it might even have been imagined that in such a solution the hydrate of silica is held in combination with an excess of acid, had Graham not obtained soluble silica perfectly free from acid, and if there were not solutions of silica free from

The hydrosol of silica prepared by mixing an excess of hydrochloric acid with a solution of sodium silicate, may be freed from the admixtures both of hydrochloric acid and salt, sodium chloride, *by means of dialysis*,[17] as *Graham* showed (in 1861) in explaining the nature of colloids, and making many other important chemical investigations. The solution, containing the acid, salt, and silica, all dissolved in water, is poured into a dialyser—that is, a vessel with a porous diaphragm surrounded by water. Certain substances pass more easily through the diaphragm than others. This may be represented thus: the passage through the diaphragm proceeds in both directions, and if the solution on each side of the diaphragm be equally strong, then there will be equal numbers of molecules of the soluble substance passing into either side in a given time, some passing quickly and others slowly. The metallic chlorides and hydrochloric acid belong to the series of crystalloids which easily pass through a diaphragm, and therefore the hydrochloric acid and sodium chloride contained in the above-mentioned dialyser pass from the solution through the diaphragm into the water of the external vessel with considerable rapidity. The aqueous solution of colloidal silica also penetrates through the diaphragm, but very much more slowly. But if the amount of the substance dissolved is not equal on either side of the diaphragm, then the whole system strives to attain a state of equilibrium; that is, the given substance penetrates through the diaphragm from the side where it abounds to the part where there is a lesser quantity of it. All substances which are soluble in water have the faculty of penetrating through a membrane swollen in water, but the velocity of penetration is not equal, and in this respect the dialyser separates substances like a sieve. The silica passes less rapidly through the diaphragm than the sodium chloride and hydrochloric acid, so that by repeatedly changing the external water it is easy to effect the extraction of the chlorine compounds from the dialyser, which will finally only contain a solution of silica. This extraction may be so complete that the liquid taken from the dialyser

any acid in nature. At all events a somewhat strong solution of free silica or silicic acid may be obtained from soluble glass diluted with water. The solution, besides silica, will contain sodium chloride and an excess of the acid taken. If this solution remains for some time exposed to the air, or in a closed vessel, and under various other conditions, it is found that, after a time, insoluble gelatinous silica separates out—that is, the soluble form of silica is unstable, like the soluble form of alumina. The analogous forms of molybdic or tungstic acids may be heated, evaporated, and kept for a long period of time without the soluble form being converted into the insoluble.

[17] See Vol. I. p. 68, Note 18. A solution of water-glass mixed with an excess of hydrochloric acid is poured into the dialyser, and the outer vessel is filled with water, which is renewed (from a water tap). The water carries off the sodium chloride and hydrochloric acid, and the hydrosol remains in the dialyser.

will not give any precipitate with a solution of silver nitrate. Graham thus obtained soluble silica having a distinctly acid reaction, which, however, disappeared on the addition of a very minute quantity of alkali; for ten parts of silica in the solution it was sufficient to take one part of alkali in order to give the liquid an alkaline reaction, so slightly energetic are the acid properties of silicic acid. The solution of silica obtained by this method becomes gelatinous in time, or on being heated, or on evaporation under the receiver of an air-pump, &c. The hydrosol is transformed into the hydrogel, the soluble hydrate into the gelatinous.

Thus in addition to the gelatinous form of the silicic acid, there exists also a variety of this substance, soluble in water, as is the case with alumina. Such variation in properties and exactly the same relations with regard to water characterise an immense series of other substances having a great significance in nature. The number of such substances is especially great among organic compounds, and particularly in those classes of them which compose the principal material of the bodies of animals and plants. It is sufficient to mention, for instance, the gelatin which is familiar to all as carpenter's and other glues, and in the form of size and jelly. The same substance is also known in the solution which is used to join objects together. In a peculiar insoluble condition it enters into the composition of hides and bones. These various forms of gelatin differ in the same way as the different varieties of silica. The property of forming a jelly is exactly the same as in silica, and the adhesiveness of the solutions of both substances is identical; soluble silica adheres like a solution of gelatin. The same properties are again shown by starch, rosin, and albumin, and by a series of similar substances. The diaphragms used in dialysis are also insoluble, gelatinous, forms of colloids. The bodies of animals and plants consist largely of similar matter, insoluble in water, corresponding with the gelatinous or insoluble silicon hydrate, or with glue. The albumin which coagulates when eggs are boiled is a typical form of the gelatinous condition of such substances in the body. These slight indications are sufficient in order to see how great is the significance of those transformations which are so sharply observable in silica. The facts discovered by *Graham* in 1861-1864 comprise the most essential acquisitions in the general association of these phenomena of nature in the history of organic forms. The facility of transit from hydrogel to hydrosol is the first condition of the possibility of the development of organisms. The blood contains hydrosols, and the hydrogels of the same substances are contained in the muscles and tissues, and especially on the surface, of the body. All tissues are formed

from the blood, and in that case the hydrosols turn into hydrogels.[18] The absence of crystallisation, the property, apparently under influence of feeble agencies, of passing from the soluble condition to the insoluble, to the gelatinous condition of the hydrogel, compose the fundamental properties of all colloids.[19]

Silica, as regards its *salt-forming properties*, stands in the series of oxides on the boundary line on the side of the acids in just such a place as alumina occupies on the side of the bases—that is, aluminium hydroxide is the representative of the feeblest bases and silicic acid is the least energetic of acids (at least in the presence of water—that is, in aqueous solutions); in alumina, however, the basic properties are distinctly expressed, while in silica the acid properties preponderate. Like all feeble acid oxides it is capable of forming, with other acids, but slightly stable saline compounds which are very easily decomposed in the presence of water, but nevertheless it does not form compounds in the presence of water with other acids, whilst alumina, although forming saline compounds with acids, is, like all feebly basic acids, at the same time capable of combining with alkalis. The chief peculiarity of the silicates consists in the number of their types. The salts formed with nitric or sulphuric acid exist in one, two, and three fairly stable forms, but for acids like silicic acid the number of forms is very great, almost unlimited. The natural silicates in particular furnish proof of this fact; they contain various bases in combination with silica, and for one and the same base there often exist various degrees of combination. As feeble bases are capable of forming basic salts in addition to normal salts—that is, a compound of a normal salt with a feeble base (either the hydroxide or the oxide)—so the feeble acid oxides (although not all) form, in addition to normal salts, highly acid salts—that is, normal salts *plus* acid (hydrate or anhydride). Such acids are boric, phosphoric, molybdic, chromic, and especially silicic, acid. These salts are all non-volatile.

[18] A similar process occurs in plants—for example, when they secrete a store of material for the following year in their bulbs, roots, &c. (for instance, the potato in its tubers), the solutions from the leaves and stems penetrate into the roots and other parts in the form of hydrosols, where they are converted into hydrogels—that is, into an insoluble form, which is acted on with difficulty and is easily kept unaltered until the period of growth—for example, until the following spring—when they are re-converted into hydrosols, and the insoluble substance re-enters into the sap, and serves as a source of the hydrogels in the leaves and other portions of plants.

[19] As regards their chemical composition the colloids are very complex—that is, have a high molecular weight and a large molecular volume—in consequence of which they do not penetrate through membranes, and are easily subject to variation in their physical and chemical properties (owing to their complex structure and polymerism?) They have but little chemical energy, and are generally feeble acids.

In order to explain these relations it is necessary first to recollect the existence of the various hydrates of silica, or silicic acids,[20] and then to turn our attention to the similarity between silicon compounds and metallic alloys. Silica is an oxide having the appearance of, and in many respects the same properties as, those oxides which combine with it, and if two metals are capable of forming a homogeneous alloy in which there exist definite or indefinite compounds, then it is lawful to assume a similar power of forming mutual alloys in the case of oxides. Such alloys are found in indefinite, amorphous masses in the form of glass, lava, slags, and a number of similar siliceous compounds which do not contain any definite types of combination, but nevertheless are homogeneous throughout their mass. By slow cooling, or under other circumstances, definite crystalline compounds may—and sometimes do

[20] This is in accordance with the generally-accepted representation of the relations between salts and the hydrates of acids, but it is of little help in the study of siliceous compounds, because (1) the hydrates are nothing else but salts of hydrogen, and, therefore, they must bear the same relation to each other as salts do; (2) the hydrate $SiO_2,2H_2O$ is almost unknown, whilst compounds of silica with a large proportion of water have long been known, and salts are known which contain a still larger relative proportion of bases. Properly speaking, it becomes necessary to explain the property of $(SiO_2)_n$ to combine with $(RO)_m$, where n may be greater than m, and where R may be H_2. There we are aided by those facts which have been attained by the investigation of carbon compounds, especially with respect to glycol. Glycol is a compound having the composition $C_2H_6O_2$, only differing from alcohol, C_2H_6O, by an extra atom of oxygen. This hydrate contains two hydroxyl groups, which may be successively replaced by chlorine, and the hydrogen of both may be successively substituted by sodium and various acid radicles. Therefore the composition of glycol should be represented as $C_2H_4(OH)_2$. It has been found that glycol forms so-called polyglycols. Their origins will be understood from the fact that glycol as a hydrate has a corresponding anhydride of the composition C_2H_4O, known as ethylene oxide. This substance is ethane, C_2H_6, in which two hydrogens are replaced by one atom of oxygen. Ethylene oxide is not the only anhydride of glycol, although it is the simplest one, because $C_2H_4O=C_2H_4(OH)_2-H_2O$. Various other anhydrides of glycol are possible, and have actually been obtained, of the composition $nC_2H_4(OH)_2-(n-1)H_2O=(C_2H_4)_nO_{n-1}(OH)_2$. These imperfect anhydrides of glycol, or *polyglycols*, still contain hydroxyls like glycol itself, and therefore are of an alcoholic character in the same degree as glycol itself. They are obtained by various methods and, amongst others, by the direct combination of ethylene oxide with glycol, because $C_2H_4(OH)_2+(n-1)C_2H_4O=(C_2H_4)_nO_{n-1}(OH)_2$. The most important circumstance, from a theoretical point of view, is that these polyethylenic glycols may be distilled without undergoing decomposition, and that the general formula given above expresses their actual molecular composition—that is, corresponds with their molecular weight. Hence we have here a direct combination of the anhydride with the hydrate, and, moreover, a repeated one. The formula A_nH_2O may express the composition of glycol and polyglycols with respect to ethylene oxide in a most simple manner, if A stand for ethylene oxide. When $n=1$ we have glycol, when n is greater than 1 a polyglycol. Such also is the relation of the salts of hydrate of silica, if A stand for silica, and if we imagine that H_2O may also be taken m times. Such a representation of the *polysilicic acids* corresponds with the representation of the polymerism of silica. Laurent supposed the existence of several polymeric forms, Si_2O_4, Si_3O_6, &c., besides silica, SiO_2. It is obvious that the letter n presupposes similar polymeric forms.

separate from this homogeneous mass, as also sometimes definite crystalline alloys separate from metallic alloys.

The formation of crystalline rocks in nature is partly of such a nature. By aqueous or igneous agency, but in any case in a liquid condition, those oxides which form the earth's crust and her crystalline minerals came into mutual contact. First of all they formed a shapeless mass, of which lava, glass, and slags are examples, but little by little, or else suddenly, some definite compounds of certain oxides existing in this alloy or in the shapeless mass were formed. This is entirely similar to two metals forming a homogeneous alloy,[21] and under known circumstances (for instance, on cooling the alloy, or in the case of aqueous solution, when the two metals are simultaneously liberated from the solution), crystalline definite compounds are separated. In any case there is no doubt that there is less distinction between silica and bases, than between bases and such anhydrides as, for instance, sulphuric or nitric, or even carbonic, as is seen on comparing the physical and chemical properties of silica and various kinds of oxides. Alumina, especially, is exceedingly near akin to silica ; not only in the hydrated state, but also in the anhydrous condition, there even exists a certain

[21] For us the latter have not a saline character, only because they are not regarded from this point of view, but an alloy of sodium and zinc is, in a wide sense, a salt in many of its reactions, for it is subject to the same double decompositions as sodium phosphide or sulphide, which clearly have saline properties. The latter, when heated with ethyl iodide, forms ethyl phosphide, and the former—*i.e.* the alloy of zinc and sodium—gives zinc ethyl; that is, the element (P, S, Zn) which was united with the sodium passes into combination with the ethyl: $RNa + EtI = REt + NaI$, hence the alloy of sodium and zinc is a saline substance in the same sense that sodium sulphide is. By combining sodium successively with chlorine, sulphur, phosphorus, arsenic, antimony, tin, and zinc we obtain substances having less and less the ordinary appearance of salts, but if the alloy of sodium and zinc cannot be termed a salt, then perhaps this name cannot be given to sodium sulphide, and the compounds of sodium with phosphorus. The following circumstance may also be observed: with chlorine, sodium gives one compound (with oxygen, at the most three), with sulphur five, with phosphorus probably still more, with antimony naturally still more, and the more analogous an element is to sodium, the more varied are the proportions in which it is able to combine with it; the less are the alterations in the properties which take place by this combination, and the nearer does the compound formed approach to the class of compounds known as indefinite chemical compounds. In this sense a siliceous alloy, containing silica and other acids, is a salt. The oxide to a certain extent plays the same part as the sodium, whilst the silica plays the part of the acid element which was taken successively by zinc, phosphorus, sulphur, &c., in the above examples. Such a comparison of the silica compounds with alloys presents the great advantage of including under one category the definite and indefinite silica compounds which are so analogous in composition—that is, brings under one head such crystalline substances as certain minerals, and such amorphous substances as are frequently met with in nature, and are artificially prepared, as glass, slags, enamels, &c.

If the compounds of silica are substances like the metallic alloys, then (1) the chemical union between the oxides of which they are composed must be a feeble one, as it is in all compounds formed between analogous substances. In reality such feeble agencies as

similarity between the crystalline forms of alumina and silica, taken separately. Both are very hard, transparent, inactive, non-volatile, infusible, and crystallise in the hexagonal system—in a word, they are remarkably similar, and for this reason they are capable, like two kindred metals, of entering into many various degrees of combination. Isomorphous mixtures—that is, the substitution of oxides akin both in their properties and chemical characters—are very frequently met with among minerals, and the study of the latter gave the principal support to the study of isomorphism. Thus, in a whole series of minerals, lime and magnesia are found in variable and interchangeable proportions. Exactly the same may be said of potassium and sodium, of alumina and ferric oxide, of manganous, ferrous, magnesium oxides, &c. Such isomorphous mixtures do not, however, extend without change of form and properties beyond certain rather narrow limits. What I mean by this is that lime is not always replaced totally, but often only in small quantities, by magnesia, or by the manganous and ferrous oxides, without changing the crystalline form. The same may be observed concerning potassium and lithium, which may be in part, but not completely, replaced by sodium. On the total substitution of one metal for another, often (although not invariably) the entire nature of the substance is changed; for instance, *enstatite* (or bronzite) is a magnesium bisilicate with a small isomorphous substitution of calcium for magnesium; its composition is expressed by the formula $MgSiO_3$, it belongs to the rhombic system. On the entire substitution of calcium, *wollastonite*, $CaSiO_3$, of the monoclinic system, is obtained; when manganese is substituted, *rhodonite*, of the triclinic system, is produced; but in all of them the angles of the prism are 86° to 88°.

It is, however, easy to imagine, and fact confirms the supposition, that in a complex siliceous compound containing, for instance, sodium

water and carbonic acid are able, although slowly, to act on and destroy the majority of the complex silica compounds in rocks, as we saw in the preceding chapter; (2) their formation, like that of alloys, should not be accompanied by a considerable alteration of volume; and this is actually the case. For example, felspar has a specific gravity of about 2·6, and therefore, taking its composition to be $K_2O,Al_2O_3,6SiO_2$, we find its volume, corresponding with this formula, to be 556·8/2·6 = 214; the volume of $K_2O = 35$, of $Al_2O_3 = 26$, and of $SiO_2 = 22·6$. Hence the sum of the volumes of the component oxides, $35 + 26 + 6 \times 22·6 = 196$, which is very nearly equal to that of the felspar; that is, its formation is attended by a slight expansion, and not by contraction, as is the case in the majority of other cases when combinations determined by strong affinities are accomplished. In the case in question the same phenomenon is observed as in solutions and alloys—that is, as in cases of feeble affinities. So also the specific gravity of glass is directly dependent on the amount of those oxides which enters into its composition. If in the preceding example we take the sp. gr. of silica to be, not 2·65, but 2·2, then its volume = 27·3, and then the sum of the volumes will be = 224—that is, greater than that of orthoclase.

and calcium, the whole of the sodium may be replaced by potassium, and *at the same time* the whole of the calcium by magnesium, because then the substitution of potassium for the sodium will produce a change in the nature of the substance contrary to that which will occur from the calcium being replaced by magnesium. That increase in weight, decrease in density, increase of chemical energy, which accompanies the exchange of sodium and potassium will, so to speak, be compensated by the exchange of calcium and magnesium, because both in weight and in properties the sum of Na + Ca is very near to the sum of K + Mg. *Pyroxene* or *augite* can be taken as an example; its composition may be expressed by the formula $CaMgSi_2O_6$; that is, it corresponds with the acid H_2SiO_3; it is a bisilicate. In many respects it closely resembles another mineral called '*spodumene*' (they are both monoclinic). This latter has the composition $Li_6Al_8Si_{15}O_{45}$. On reducing both formulæ to an equal contents of silica the following distinction will be observed between them: spodumene $(Li_2O)_6(Al_2O_3)_8 30SiO_2$; augite $(CaO)_{15}(MgO)_{15}30SiO_2$.[22] That is, the difference between them consists in the sum of the magnesia and lime $(MgO)_{15} + (CaO)_{15}$ replacing the sum of the lithium oxide and alumina $(Li_2O)_6 + (Al_2O_3)_8$; and in the chemical relation these sums are near to one another, because magnesium and calcium, both in forms of oxidation and in energy (as bases), in all respects occupy the mean between lithium and aluminium, and therefore the sum of the first may be replaced by the sum of the second.[23]

[22] If we take the composition of spodumene, as it is often represented to be, $Li_2O,Al_2O_3,4SiO_2$, then the corresponding formula of augite will be $(CaO)_2,(MgO)_2,4SiO_2$, and also the amount of oxygen in the sum of $Li_2OAl_2O_3$ will be the same as in $(CaO)_2(MgO)_2$. I may remark, for the sake of clearness, that lithium belongs to the first, aluminium to the third group, and calcium and magnesium to the intermediate second group; lithium, like calcium, belongs to the even series, and magnesium and aluminium to the uneven.

The representation of the substitutions of analogous compounds here introduced was first deduced by me in 1856. It finds much confirmation in facts which have been subsequently discovered—for example, with respect to tourmalin. Wülfing (1888), on the basis of a number of analyses (especially of those by Riggs), states that all its varieties contain an isomorphous mixture of alkali and magnesia tourmalin; into the composition of the former there enters $12SiO_2,3B_2O_3,8Al_2O_3,2Na_2O,4H_2O$, and of the latter $12SiO_2,3B_2O_3,5Al_2O_3,12MgO,3H_2O$. Hence it is seen that the former differs by the sum of $3Al_2O_5,2Na_2O,H_2O$, and that in the latter this sum of oxides is replaced by 12MgO, in which there is as much oxygen as in the complement of the more sharply-defined base $2Na_2O$ and less basic $3Al_2O_3H_2O$—that is, the relation is just the same here as between augite and spodumene.

[23] With respect to the silica compounds of the various oxides, it must be observed that only the *alkali salts* are known in a soluble form; all the others only exist in an insoluble form, so that a solution of the alkali compounds of silica, or soluble glass, gives a precipitate with a solution of the salts of the majority of other metals, and this precipitate will contain the silica compounds of the other bases. The silica compounds of the alkalis may be obtained by a dry or wet method by fusing the alkalis or their car-

The most remarkable complex siliceous compounds are the *felspars*, which enter into nearly all the primary rocks like porphyry, granite,

bonates with silica, or by dissolving the hydrates of silica in the caustic alkalis, as has been already mentioned. The maximum amount of the gelatinous hydrate of silica, which dissolves in caustic potash, corresponds with the formation of a compound, $2K_2O,9SiO_2$. But this compound is already insoluble in cold water, and is partially decomposed, with the precipitation of hydrate of silica, on cooling the solution. Solutions containing a smaller amount of silica may be kept for an indefinite time without decomposing, and silica does not separate out from the solution; but in this case a definite compound is rarely obtained, because such compounds crystallise from the solutions with difficulty. However, a crystalline bisilicate (with water) has been obtained for sodium having the composition Na_2O,SiO_2—*i.e.*, corresponding to metasilicic acid, $SiO(OH)_2$. The whole of the carbonic acid is evolved, and a similar sodium metasilicate is obtained on fusing 3·5 parts of sodium carbonate with 2 parts of silica. If less silica is taken, a portion of the sodium carbonate remains undecomposed; however, a substance may then be obtained of the composition $Si(ONa)_4$, corresponding with orthosilicic acid. It contains the maximum amount of sodium oxide capable of combining with silica under fusion. It is a sodium orthosilicate, $(Na_2O)_2,SiO_2$. There are higher degrees of combination; thus, even tetrasilicate, $Na_2O,4SiO_2$, is known in solution. If in fusing with sodium carbonate a larger proportion of silica is taken than is required for the formation of the metasilicate, then nevertheless all the silica passes into the alloy, although the resultant mass is less fusible and less soluble in water, but still it is homogeneous. Alkaline solutions, saturated with silica and known as *soluble glass*, are prepared on a large scale for technical purposes by the action of potassium (or sodium) hydroxide in a steam boiler on tripoli or infusorial earth, which contains a large proportion of amorphous silica. Solutions of the alkaline silicates have all an alkaline reaction, and are even decomposed by carbonic acid. They are chiefly used by the dyer, for the same purposes as sodium aluminate, and also for giving a hardness and polish to stucco and other cements, and in general to substances which contain lime. A lump of chalk when immersed in soluble glass, or, better still, when moistened with a solution and afterwards washed in water (or, better, in hydrofluosilicic acid, in order to bind together the free alkali and make it insoluble), becomes exceedingly hard and loses its friability, and is rendered cohesive, and cannot be levigated in water. This transformation is due to the fact that the hydrate of silica present in the solution acts upon the lime, forming a stony mass of calcium silicate, whilst the carbonic acid previously in combination with the lime enters into combination with the alkali and is washed away by the water.

Calcium carbonate, and the carbonates of the alkaline earths in general, also evolve all their carbonic acid when heated with silica, and in some instances even form somewhat fusible alloys. Lime forms a fusible slag of *calcium silicate*, of the composition CaO,SiO_2 and $2CaO,3SiO_2$. With a larger proportion of silica the slags are infusible in a furnace. The magnesium *slags* are less fusible than those with lime, and are often formed in smelting metals. Many compounds of the metals of the alkaline earths with silica are also met with in nature. For instance, among the magnesium compounds there is *olivine*, $(MgO)_2,SiO_2$, sp. gr. 3·4, which occurs in meteorites, and sometimes forms a precious stone (peridote), and occurs in slags and basalts. It is decomposed by acids, is infusible before the blow-pipe, and crystallises in the rhombic system. *Serpentine* has the composition $3MgO,2SiO_2,2H_2O$; it sometimes forms whole mountains, and is distinguished for its great cohesiveness, and is therefore used for building purposes. It is generally tinted green; its specific gravity is 2·5; it is exceedingly infusible, even before the blow-pipe. It is acted on by acids. Among the magnesium compounds of silica, *talc* is very widely used. It is frequently met with in rocks which are widely distributed in nature, and sometimes in compact masses; it writes like a slate pencil or chalk, and is greasy to the touch, and is therefore also known as *steatite*. It crystallises in the rhombic system, and resembles mica in many respects; like it, it is divisible into laminæ,

gneiss, &c. These felspars always contain, in addition to silica and alumina, oxides presenting more marked basic properties, such as potash, soda, and lime. Thus the *orthoclase* (adularia), or ordinary felspar (monoclinic) of the granites, contains $K_2O,Al_2O_3,6SiO_2$; *albite* contains the same substances, only with Na_2O instead of K_2O (it already appertains to the triclinic system); *anorthite* contains lime, and its composition is $CaO,Al_2O_3,2SiO_2$. On expressing the two latter in equal terms of oxygen, we have :—

Albite	Na_2	Al_2	Si_6	O_{16}
Anorthite	Ca_2	Al_4	Si_4	O_{16}

It is, then, evident that on albite turning into anorthite Na_2Si_2 is replaced by Ca_2Al_2, and this sum, both in chemical energy and in form of oxide, may be counted as corresponding with the first, because sodium and silicon are extreme elements in chemical character (from groups I. and IV.), and calcium and aluminium are means between them (from groups II. and III.), and actually both these felspar minerals are not only of one (triclinic) system, but form (Tschermak, Schuster), judging from their composition and all their properties, all possible kinds of definite compounds (isomorphous mixtures) between

greasy to the touch, and having a sp. gr. 2·7. These laminæ are very soft, lustrous, and transparent, and are infusible and insoluble in acids. The composition of talc approaches nearly to $6MgO,5SiO_2,2H_2O$.

Among the crystalline silicates the following minerals are known:—*Wollastonite* (tabular-spar), crystallises in the monoclinic system; sp. gr. 2·8; it is semi-transparent, difficultly fusible, decomposed by acids, and has the composition of a metasilicate, $CaOSiO_2$. But isomorphous mixtures of calcium and magnesium silicates occur with particular frequency in nature. The *augites* (sp. gr. 3·3), diallages, hypersthenes, hornblendes (sp. gr. 3·1), amphiboles, common asbestos, and many similar minerals, sometimes forming the essential parts of entire rock formations, contain various relative proportions of the bisilicates of calcium and magnesium partially mixed with other metallic silicates, and generally anhydrous, or only containing a small amount of water. Many of these minerals present a composition in which there are equal atomic amounts of lime and magnesia, and sufficient silica to form a metasilicate—that is, their composition approaches to the formula $MgO,CaO,2SiO_2$; but sometimes a considerable proportion of alumina also enters into their composition, and still more often the amount of silica exceeds that given in the above formula. In the pyroxenes, as a rule, the lime predominates, and in the amphiboles (also of the monoclinic system) the magnesia predominates.

Clay is one of the hydrous silicates of alumina, $(Al_2O_3)_m(SiO_2)_n$. These are all infusible at a furnace heat, or only soften with difficulty. The most easily softened is the compound containing $2Al_2O_3,9SiO_2$ (trisilicate). In an anhydrous state in nature there are known, for example, the *staurolites*, of the rhombic system, hard as quartz, sp. gr. 3·7, $3R_2O_3,2SiO_2$, where R is aluminium partially replaced by iron in the form of ferrous and ferric oxides. This is almost a semi-silicate, because it contains O_4 in the form of silica to O_9 in the form of alumina, and we may remark that more energetic bases do not give such lower degrees of combination with silica and such basic salts, and we know that the faculty to form such salts is clearly developed in alumina.

themselves. Thus oligoclase, andesine, labradorite, &c. (plagioclases), are nothing more than mutual combinations of albite and anorthite. Thus albite, $Na_2O,Al_2O_3,6SiO_2$, enters into the composition of labradorite in combination with one to two parts of anorthite $(CaO)_2(Al_2O_3)_2(SiO_2)_4$. The class of *zeolites* corresponds to the felspars; they are hydrated compounds of a similar composition to the felspars. Thus *natrolite* contains $Na_2O,Al_2O_3,3SiO_2,2H_2O$, and *analcime* presents the same composition, but contains $4SiO_2$ instead of $3SiO_2$. In general, the felspars and zeolites contain $RO,Al_2O_3,nSiO_2$, where n varies considerably.[24]

Such complex silicates, containing all other bases except alkalis, are generally insoluble in water,[25] and if they undergo change in it, it is

[24] The majority of the siliceous minerals have now been obtained artificially under various conditions. Thus N. N. Sokoloff showed that slags very frequently contain peridote. Hautefeuille, Chroustchoff, Friedel, and Sarasin obtained felspar identical in all respects with the natural minerals. The details of the methods here employed must be looked for in special works on mineralogy; but, as an example, we will describe the method of the preparation of felspar employed by Friedel and Sarasin (1881). From the fact that felspar gives up potassium silicate to water even at the ordinary temperature (Debray's experiments), they concluded that the felspar in granites had an aqueous origin (and this may be supposed to be the case from geological data); then, in the first place, its formation could not be accomplished unless in the presence of an excess of a solution of potassium silicate. In order to render this argument clear I may mention, as an example, that carnallite is decomposed by water into easily soluble magnesium chloride and potassium chloride, and therefore if it is of aqueous origin it could not be formed otherwise than from a solution containing an excess of magnesium chloride, and, in the second place, from a strongly-heated solution; again, felspar itself and its fellow components in granites are anhydrous. On these facts they based their experiments of heating hydrates of silica with alumina and a solution of potassium silicate in a closed vessel. The mixture was placed in a tightly-closed platinum tube, which was placed in a steel tube and heated to dull redness. When the mixture contained an excess of silica the residue contained many crystals of rock crystal and tridymite, together with a powder of felspar, which formed the main product of the reaction when the proportion of hydrate of silica was decreased, and a mixture of a solution of potassium silicate with alumina precipitated together with the silica by mixing soluble glass with aluminium chloride was employed. The composition, properties, and forms of the resultant felspar proved it to be identical with that found in nature. The experiments approach very nearly to the natural conditions, all the more as felspar and quartz are obtained in one mixture, as they so often occur together in nature.

[25] The application of *cements* is based on this principle; they are those sorts of lime which generally form a stony mass, which even hardens under water, when mixed with sand and water.

The hydraulic properties of cements are due to their containing calcareous and silico-aluminous compounds which are able to combine with water and form hydrates, which are then unacted on by water. This is best proved, in the first place, by the fact that certain slags containing lime and silica, and obtained by fusion (for example, in blast-furnaces), solidify like cements when finely ground and mixed with water; and, in the second place, by the method now employed for the manufacture of artificial cements (formerly only particular and comparatively rare natural products were used). For this purpose a mixture of lime and clay is taken, containing about 25 p.c. of the latter; this mixture is then heated, not to fusion, but until the carbonic anhydride and water con-

but very slow, and more often only in the presence of carbonic acid. Some of the silicates which are insoluble in water are easily and directly decomposed by acids; for instance, the zeolites and those fused silicates which contain a large quantity of energetic bases—such as lime. Many of the silicates, like glass,[26] are not changed by the action of

tained in the clay is expelled. This mass when finely ground forms Portland cement, which hardens under water. The process of hardening is based on the formation of chemical compounds between the lime, silica, alumina, and water. These substances are also found combined together in various natural minerals—for example, in the zeolites, as we saw above. At all events the hardened cement contains a considerable amount of water, and its hardening is naturally due to hydration—that is, to the formation of compounds with water. Well-prepared and very finely-ground cement is able to harden comparatively quickly (in several days, especially after being rammed down), with 3 parts (and even more) of coarse sand and with water, into a stony mass which is as hard and durable as many stones, and more so than bricks and limestone. Hence not only all maritime constructions (docks, ports, bridges, &c.), but also ordinary buildings, are made of Portland cement, and are distinguished for their great durability. A combination of ironwork (ties, girders) and cement is particularly suitable for the construction of aqueducts, arches, reservoirs, &c. The thickness of the arches and walls made of such cements may be much less than those built up of ordinary stone. Hence the production and use of cement rapidly increases from year to year. The origin of accurate data respecting cements is chiefly due to Vicat. In Russia Professor Schuliachenko has greatly aided the extension of accurate data concerning Portland cement. Many works for the manufacture of cement have already been established in various parts of Russia, and this production promises a great future in the arts of construction.

[26] *Glass* presents a similar complex composition, like that of many minerals. The ordinary sorts of white glass contain about 75 p.c. of silica, from 10 to 15 p.c., and even more, of sodium oxide, and 7 to 20 p.c. of lime; but the lower sorts of glass sometimes contain up to 10 p.c. of alumina. The mixtures which are used for the manufacture of glass are also most varied. They take, for example, about 300 parts of pure sand, about 100 parts of sodium carbonate, and 50 of limestone, which is sometimes taken in double this proportion. Ordinary *soda-glass* contains sodium oxide, lime, and silica as the chief component parts. It is generally prepared from sodium sulphate mixed with charcoal, silica, and lime (Chapter XII.), in which case the following reaction takes place at a high temperature: $Na_2SO_4 + C + SiO_2 = Na_2SiO_3 + SO_2 + CO$. Sometimes potassium carbonate is taken for the preparation of the better qualities of glass. In this case a glass, *potash-glass*, is obtained containing potassium oxide instead of sodium oxide. The best-known of these glasses is the so-called Bohemian glass or crystal, which is prepared by the fusion of 50 parts of potassium carbonate, 15 parts of lime, and 100 parts of quartz. The preceding kinds of glass contain lime, whilst crystal glass contains lead oxide instead. Flint glass—that is, the lead glass used for optical instruments—is prepared in this manner, naturally from the purest possible materials. *Crystal glass—i.e.* glass containing lead oxide—is softer than ordinary glass, but, on the other hand, it is more fusible and has a higher index of refraction. The lower qualities of glass—for example, bottle-glass—are prepared from unsorted and impure materials, and therefore contain, besides the colourless oxides, other substances and iron oxides, which communicate different tints to the glass. However, although the materials for the preparation of glass be most carefully sorted, a certain amount of iron oxides falls into the glass and renders it greenish. This coloration may be destroyed by adding a number of substances to the glassy mass, which are able to convert the ferrous oxide into ferric oxide; for example, manganese peroxide (because the peroxide is deoxidised to manganous oxide, which only gives a pale violet tint to the glass) and arsenious anhydride, which is deoxidised to arsenic, which is volatilised. The manufacture of glass is carried on in furnaces giving a very high tem-

acids, particularly if they contain much acid oxide (silica), whilst fusion with alkalis leads to the formation of compounds rich in bases, after which acids decompose the alloys formed.[27]

According to the periodic law, the nearest analogues of silicon ought to be elements of the uneven series, because silicon, like sodium, magnesium, and aluminium, belongs to the uneven series.[28] Immediately

perature (often in regenerative furnaces, Chapter IX.). Large clay crucibles are placed in these furnaces, and the mixture destined for the preparation of the glass, having been first roasted, is charged into the crucibles. The temperature of the furnace is then gradually raised. The process is attended by three separate periods. At first the mass intermixes and begins to react; then it fuses, and evolves carbonic acid gas, and forms a molten mass; and, lastly, at the highest temperature, it becomes homogeneous and quite liquid, which is necessary for the ultimate elimination of the carbonic anhydride and solid impurities, which then collect at the bottom of the crucible. The temperature is then somewhat lowered, and the glass is taken out on tubes and blown into objects of various shapes. In the manufacture of window-glass it is blown into large cylinders, which are then cut at the ends and across, and afterwards bent back in a furnace into the ordinary sheets. After being worked up, all glass objects have to be subjected to a slow cooling (*annealing*) in special furnaces, as otherwise they are very brittle, as is seen in the so-called 'Rupert's drops,' formed by dropping molten glass into water; although these drops preserve their form, they are so brittle that they break up into a fine powder if a small piece be knocked off them. Then glass objects have frequently to be polished and chased. In the manufacture of mirrors and many massive objects the glass is cast and then ground and polished. Coloured glasses are made either by directly introducing various oxides, which give their characteristic tints into the glass itself, or a thin layer of a coloured glass is laid on the surface of ordinary glass. Green glasses are formed by the oxides of chromium and copper, blue glasses by cobalt oxide, violet glasses by manganese oxide, and red glass by cuprous oxide and by the so-called purple of cassius—*i.e.* a compound of gold and tin—which will be described later. A yellow coloration is obtained by means of the oxides of iron, silver, or antimony, and also by means of carbon, especially for the brown tints for certain kinds of bottle-glass.

From what has been said about glass it will be understood that it is impossible to give a definite formula for it, because it is a non-crystalline or amorphous alloy of silicates; but such an alloy can only be formed within certain limits in the proportions between the component oxides. With a large proportion of silica the glass very easily becomes clouded when heated; with a considerable proportion of alkalis it is easily acted on by moisture, and becomes cloudy in time on exposure to the air; with a large proportion of lime it becomes infusible and opaque, owing to the formation of crystalline compounds in it; in a word, a certain proportion is practically attained among the component oxides in order that the glass formed may have suitable properties. Nevertheless, it may be well to remark that the composition of common glass approaches to the formula $Na_2O,CaO,4SiO_2$.

The coefficient of cubical expansion of glass is nearly equal to that of platinum and iron, being approximately 0·000027. The specific heat of glass is nearly 0·18, and the specific gravity of common soda glass is nearly 2·5, of Bohemian glass 2·4, and of bottle glass 2·7. Flint glass is much heavier than common glass, because it contains the heavier oxide of lead, its specific gravity being 2·9 to 3·2.

[27] It must be recollected that although acids seem to act only feebly on the majority of silicates, nevertheless a finely-levigated powder of siliceous compounds is acted on by strong acids, especially with the aid of heat, the basic oxides being taken up and gelatinous silica left behind. In this respect sulphuric acid heated to 200° with finely-divided siliceous compounds in a closed tube evinces the most energetic action.

[28] Such elements as silicon, tin, and lead were only brought together under one common

after silicon follows ekasilicon or *germanium*, Ge=72, whose properties were predicted (1871) before Winkler (1886) in Freiberg, Saxony (p. 24), discovered this element in a peculiar silver ore called *argyrodite*.[29] Easily reduced from the oxide by heating with hydrogen and charcoal, and separated from its solutions by zinc, metallic germanium proved to be grayish white, easily crystallisable (in octahedra), brittle, fusible (under a coating of fused borax) at about 900°, and easily oxidisable; the specific gravity=5·469, the volume weight=72·3, and the specific heat=0·076,[30] as might be expected for this element according to the periodic law. The corresponding *germanium dioxide*, GeO_2, is a white powder having a specific gravity of 4·703; water, especially boiling water, dissolves this dioxide (1 part of GeO_2 requires for solution 247 parts of water at 20°, 95 parts at 100°). It forms soluble salts with alkalis and is but sparingly soluble in acids.[31] In a stream of chlorine the metal forms *germanium chloride*, $GeCl_4$, which boils at 86°, and has a specific gravity of =1·887 at 18°; water decomposes it, forming the oxide. All these properties[32] of germanium, showing its analogy to silicon and tin, form a most beautiful demonstration of the truth of the periodic law.[33]

group by means of the periodic law, although the quadrivalency of tin and lead was known much earlier. Generally silicon was placed among the non-metals, and tin and lead among the metals.

[29] At first (February 1886) the want of material to work on, the absence of a spectrum in the Bunsen's flame, and the solubility of many of the compounds of germanium, presented difficulties in the researches of Professor Winkler, who, on analysing argyrodite by the usual method, obtained a constant loss of 7 p. c., and was thus led to search for a new element. The presence of arsenic and antimony in the accompanying minerals also impeded the separation of the new metal. After fusion with sulphur and sodium carbonate, argyrodite gives a solution of a sulphide which is precipitated by an *excess* of hydrochloric acid; germanium sulphide is soluble in ammonia and then precipitated by hydrochloric acid, as a *white* precipitate, which is dissolved (or decomposed) by water. The composition of argyrodite is $(Ag_2S)_3GeS_2$, it contains by analysis 6·9 p. c. of germanium, whilst the formula requires 8·2 p. c.; the difference is explained by the presence of iron, zinc, and mercury. When the mineral is heated in a current of air it forms sulphurous anhydride and a sublimate of germanium sulphide, GeS_2. After being oxidised by nitric acid, dried and ignited, this leaves the oxide GeO_2, which is reduced to the metal when ignited in a stream of hydrogen.

[30] G. Kobb determined the spark spectrum of germanium, when the metal was taken as one of the electrodes of a powerful Ruhmkorff's coil. The wave lengths of the most distinct lines are 602, 583, 518, 513, 481, 474.

[31] If germanium or germanium sulphide be heated in a stream of hydrochloric acid, it forms a volatile liquid, which boils at 72°, and which Winkler regarded as germanium chloride, $GeCl_2$, or germanium chloroform, $GeHCl_3$. It is decomposed by water, forming a white substance, which perhaps may be the hydrate of germanious oxide, GeO, and acts as a powerfully reducing agent in a hydrochloric acid solution.

[32] Even the fact that under certain circumstances germanium gives a blue coloration like that of ultramarine, as Winkler showed, and as might be expected from the analogy of germanium with silicon.

[33] Winkler expressed this in the following words (*Jour. f. pract. Chemie*, 1886 [2], 34, 182–183): '. . . . es kann keinem Zweifel mehr unterliegen, dass das neue Element nichts

The increase of atomic weight from silicon 28 to germanium 72 is 44—that is, about the same difference as there is in the atomic weights of chlorine and bromine; between germanium and its next analogue, *tin* (Sn=118), the difference is 46—that is, almost as much as the amount by which the atomic weight of iodine exceeds that of bromine.

Tin is rarely met with *in nature*; it occurs in the veins of ancient formations, almost exclusively in the form of oxide, SnO_2, called *tin-stone*. The best known tin deposits are in Cornwall and in Malacca. In Russia tin ores have been found in small quantities on the shores of Lake Ladoga, in Pitkarand. The crushed ore may easily be separated from the earthy matter accompanying it by washing on inclined tables, as the tin-stone has a specific gravity of 6·9, whilst the impurities are much lighter. *Tin oxide is very easily reduced* to metallic tin by heating with charcoal. For this reason tin was known in ancient times, and the Phœnicians exported it from England. Metallic tin is cast into ingots of considerable weight. Tin has a white colour, but rather duller than that of silver. Tin easily fuses at 230°, and crystallises on cooling. Its specific gravity is 7·29. The crystalline structure of ordinary tin is noticed in bending tin rods, when a peculiar sound is heard, produced by the fracture of the particles of tin along the surfaces of crystalline structure.

When pure tin is considerably cooled it splits up into separate crystals, the bond between the particles is lost, the tin assumes a grey colour, becomes less brilliant—in a word, its properties become changed, as Fritzsche showed. This depends on the peculiar structure which the tin then acquires, and is particularly remarkable because it is effected by cold in a solid. If such tin be fused, or even simply heated, it becomes like ordinary tin, but is again changed when cooled. When in this condition tin has a specific gravity of 7·19. Similarly, tin is obtained by the action of the galvanic current on a solution of tin chloride; it then appears in crystals of the cubic system, and has a specific gravity of 7·18—that is, the same as when cooled.

Tin is softer than silver and gold, and is only surpassed by lead in this respect. In addition to this it is very ductile, but its tenacity is

Anderes, als das vor fünfzehn Jahren von *Mendeléeff* prognosticirte *Ekasilicium* ist.'

'Denn einen schlagenderen Beweis für die Richtigkeit der Lehre von der Periodicität der Elemente, als den, welchen die Verkörperung des bisher hypothetischen "Ekasilicium" in sich schliesst, kann es kaum geben, und er bildet in Wahrheit mehr, als die blasse Bestätigung einer kühn aufgestellten Theorie, er bedeutet eine eminente Erweiterung des chemischen Gesichtfeldes, einen mächtigen Schritt ins Reich der Erkenntniss.'

very slight, so that wire made from it will bear but little strain. In consequence of its ductility it is easily worked, by forging and rolling into very thin sheets (tin foil), which are used for wrapping many articles to preserve them from moisture, &c. In this case, however, and in many others, lead is mixed with the tin, which, within certain limits, does not alter the ductility. Whilst so soft at the ordinary temperatures tin becomes brittle at 200°, before fusing. Tin powder may be easily obtained, if tin be heated until fusion and then stirred whilst cooling. At a white heat tin may be distilled, but with more difficulty than zinc. If molten tin comes into contact with oxygen, it oxidises, forming stannic oxide, SnO_2, *and its vapour burns* with a white flame. *At ordinary temperatures tin does not oxidise*, and this very important property of tin allows it to be applied in many cases for covering other metals to prevent their oxidising. This is termed *tinning*. Iron and copper are tinned. Iron and steel sheets, coated with tin, bear the name of tin plate (for the most part made in England), and are used for numerous purposes. Tin plate is prepared by immersing iron sheets, previously thoroughly cleansed by acid and mechanical means, into molten *tin*.[34]

Tin with copper forms *bronze*, an alloy which is most extensively used in the arts. Bronze has various colours and a variety of physical properties, according to the relative amount of copper and tin which it contains. With an excess of copper the alloy has a yellow colour; the admixture of tin imparts considerable hardness and elasticity to the copper. An alloy containing 78 parts of copper and about 22 per cent. of tin is so elastic that it is used for casting bells, which naturally require a very elastic and hard alloy.[35] For casting

[34] If after this the coating of tin be rapidly cooled—for instance, by dashing water over it—it crystallises into diverse star-shaped figures, which become visible when the sheets are first immersed in dilute aqua regia and then in a solution of caustic soda.

The coating of iron by tin guards it against the direct access of air, but it only preserves the iron from oxidation so long as it forms a perfectly continuous coating. If the iron is left bare in certain places, it will be powerfully oxidised at these spots, because the tin is electro-negative with respect to the iron, and thus the oxidation is entirely limited to the iron in the presence of tin. Therefore a coating of tin over iron objects only partially preserves them from rusting. In this respect a coating of zinc is more effectual. However, a dense and invariable alloy is formed over the surface of contact of the iron and tin, which binds the coating of tin to the remaining mass of the iron. Tin may be fused with cast iron, and gives a greyish-white alloy, which is very easily cast and is used for casting many objects for which iron by itself would be unsuitable owing to its ready oxidisability and porosity. The coating of copper objects by tin is generally done to preserve the copper from the action of acid liquids, which would attack the copper in the presence of air and convert it into soluble salts. Tin is not acted on in this manner, and therefore copper vessels for the preparation of food should be tinned.

[35] The ancient Chinese alloys, containing about 20 p.c. of tin (specific gravity of alloys about 8·2) and which have been rapidly cooled, are distinguished for their resonance and elasticity. These alloys used to be manufactured in large quantities in China for the

statues and various large or small ornamental articles alloys containing 2 to 5 p. c. of tin, 10 to 30 p. c. of zinc, and 65 to 85 p. c. of copper are used.[36] Tin is also used (most often alloyed with lead) for making various objects—for instance, drinking vessels.

When heated, tin decomposes the vapour of water, liberating the hydrogen and forming stannic oxide. Sulphuric acid, diluted with a considerable quantity of water, does not act, or at all events acts very slightly, on tin, but tin reduces hot, strong, sulphuric acid, when not only sulphurous anhydride but also sulphuretted hydrogen is evolved. Hydrochloric acid acts very easily on tin, with evolution of hydrogen and formation of stannous chloride, $SnCl_2$, in solution, which, with an excess of hydrochloric acid and access of air, is converted into stannic

musical instruments known as *gong-gongs*. Owing to their hardness, alloys of this nature are also employed for casting guns, sockets, &c., and an alloy containing about 11 p.c. of tin (corresponding with the ratio $Cu_{15}Sn$) is known as gun-metal. The addition of a small quantity of phosphorus, up to 2 p.c., renders bronze still harder and more elastic, and the alloy so formed is now used under the name of phosphor-bronze.

The alloy $SnCu_3$ is brittle, of a bluish colour, and has nothing in common with either copper or tin in its appearance or properties. It remains perfectly homogeneous on cooling, and acquires a crystalline structure (Riche). All these signs clearly indicate that the alloy $SnCu_3$ is a product of chemical combination, which is also seen to be the case from its density, 8·91. Had there been no contraction, the density of the alloy would be 8·21. It is the heaviest of all the alloys of tin and copper, because the density of tin is 7·29 and of copper 8·8. The alloy $SnCu_4$, specific gravity 8·77, has similar properties. All the alloys except $SnCu_3$ and $SnCu_4$ split up on cooling; a portion richer in copper solidifies first (this phenomenon is termed the *liquation* of an alloy), but the above two alloys do not split up on cooling. In these and many similar facts we can clearly distinguish a *chemical union between the metals* forming an alloy. The alloys of tin and copper were known in very remote ages, before iron was used. The alloys of zinc and tin are less used, but alloys composed of zinc, tin, and copper frequently replace the more costly bronze.

[36] An excellent proof of the fact that alloys and solutions are subject to law is given, amongst others, by the application of Raoult's method (Vol. I. pp. 90 and 323) to solutions of different metals in tin. Thus Heycock and Neville (1889) showed that the temperature of solidification of molten tin (226·4°) is lowered by the presence of a small quantity of other metals in proportion to the concentration of the solution. The following were the reductions of the temperature of solidification of tin obtained by dissolving in it atomic proportions of different metals (for example, 65 parts of zinc), in 11800 parts of tin: Zn 2·53°, Cu 2·47°, Ag 2·67°, Cd 2·16°, Pb 2·22°, Hg 2·8°, Sb 2°, Al 1·34. As Raoult's method (Vol. I. p. 323) enables the molecular weight to be determined, the almost perfect identity of the resultant figures (except for aluminium) shows that the molecules of copper, silver, lead, and antimony contain *one atom in the molecule*, like zinc, mercury, and cadmium. It should here be mentioned that Ramsay (1889) for the same purpose (the determination of the molecular weight of metals on the basis of their mutual solution) took advantage of the variation of the vapour tension of mercury (*see* Vol. I. p. 134), containing various metals in solution, and he also found that the above-mentioned metals contain but one atom in the molecule. However, both methods are based on laws concerning the magnitudes of i (Chapter I. Notes 12 and 49), which have only been lately discovered, are not yet sufficiently explained, and require still further development before they can acquire as great a significance as the vapour density has received in the determination of the molecular weight of a metal.

chloride: $SnCl_2 + 2HCl + O = SnCl_4 + H_2O$. The action of a mixture of hydrochloric acid and tin forms an excellent means of reducing, wherein both the hydrogen liberated by the mixture (at the moment of separation) and the stannous chloride act as powerful reducing and deoxidising agents. Thus, for instance, by this mixture nitro-compounds are transformed into amido compounds—that is, the elements of the group, NO_2, are reduced to NH_2. Nitric acid diluted with a considerable quantity of water dissolves tin at the ordinary temperature, whilst the nitric acid itself is reduced, forming, amongst other things, ammonia and hydroxylamine. Here the tin passes into solution in the form of stannous nitrate. Stronger nitric acid (also the more dilute when heated) transforms the tin into its highest degree of oxidation, SnO_2, but the latter then appears as the so-called metastannic acid, which does not dissolve in nitric acid, and therefore the tin does not pass into solution. Feeble acids—for instance, carbonic and organic acids—do not act on tin even in the presence of oxygen, because tin does not form any powerful bases.

It is important to remark as a characteristic of tin that it is reduced from its solutions by many metals which are more easily oxidised, as, for instance, by zinc.

In combination, tin appears in the two types, SnX_4 and SnX_2,[37] compounds of the intermediate type, Sn_2X_6, being also known, but these latter pass with remarkable facility in most cases into compounds of the higher and lower types, and therefore the form SnX_3 cannot be considered as independent.

Stannous oxide, SnO, in an anhydrous condition is obtained by boiling solutions of stannous salts with alkalis, the first action of the alkali being to precipitate a white hydrate of stannous oxide, $Sn(OH)_2SnO$. The latter when heated parts with water as easily as the hydrate of copper oxide. In this form stannous oxide is a black crystalline powder (specific gravity 6·7, atomic volume=20) capable of further oxidation when heated. The hydrate is freely soluble in acids, and also in potassium and sodium hydroxides, but not in aqueous ammonia.[38]

[37] Many volatile compounds of tin are known, which enables their molecular weights to be established from their vapour densities. Among these may be mentioned stannic chloride, $SnCl_4$, and stannic ethide, $Sn(C_2H_5)_4$ (the latter boils at about 150°). But Meyer found the vapour density of stannous chloride, $SnCl_2$, to be variable between its boiling point (606°) and 1100°, owing, it would seem, to the fact that the molecule then varies from Sn_2Cl_4 to $SnCl_2$, but the vapour density proved to be less than that indicated by the first and greater than that shown by the second formula, although it approaches to the latter as the temperature rises—that is, it presents a similar phenomenon to that observed in the passage of N_2O_4 into NO_2 (Vol. I. p. 274).

[38] When rapidly boiled, an alkaline solution of stannous oxide deposits tin and forms stannic oxide, $2SnO = Sn + SnO_4$, which remains in the alkaline solution.

This property recalls the feeble basic properties of this lower oxide, which acts in many cases as a reducing agent.[39]

Among the compounds corresponding with stannous oxide the most remarkable and the one most frequently used is stannous chloride or chloride of tin, $SnCl_2$, also called protochloride of tin. It is a transparent, colourless, crystalline substance, melting at 250° and boiling at 606°. Water dissolves it, without visible change (in reality partial decomposition occurs, as the sequel will show). It is also soluble in alcohol. It is obtained by heating tin in dry hydrochloric acid gas, the hydrogen being then liberated, or by dissolving metallic tin in strong hot hydrochloric acid and then evaporating quickly. Crystals of the monoclinic system are then obtained having the composition, $SnCl_2,2H_2O$. An aqueous solution of this substance absorbs oxygen from the atmosphere, and gives a precipitate containing stannic oxide. This naturally means that a solution of stannous chloride will act as a reducing agent, and this fact is frequently made use of in chemical investigations—for instance, for reducing metals from their solutions—because even mercury may be reduced to a metallic state from its salts by means of stannous chloride. This reducing property is also employed in practice, especially in the dyeing industry, where this substance in the form of a crystalline salt finds an extensive application, and is known as *tin salt*.

Stannic oxide, SnO_2, found in nature (as *tinstone*, *cassiterite*), is formed during the oxidation or combustion of heated tin in air as a white or yellowish powder which fuses with difficulty. It is prepared in large quantities, because it is used in a white vitreous mixture for

[39] Weber (1882) by precipitating a solution of stannous chloride with sodium sulphite (this salt as a reducing agent prevents the oxidation of the stannous compound) and dissolving the washed precipitate in nitric acid, obtained crystals of *stannous nitrate*, $Sn(NO_3)_2,20H_2O$ on refrigerating the solution. This crystallo-hydrate easily melts, and is deliquescent. Besides this, a more stable anhydrous basic salt, $Sn(NO_3)_2,SnO$, is easily formed. In general, stannous oxide as a feeble base easily forms basic salts, just as cupric and lead oxides do. For the same reason SnX_2 easily forms double salts. Thus a potassium salt, SnK_2Cl_4,H_2O, and especially an ammonium salt, $Sn(NH_4)_2Cl_4,H_2O$, called *pink salt*, are known. Some of these salts are used in the arts, owing to their being more stable than tin salts alone. Stannous bromide and iodide, $SnBr_2$ and SnI_2, resemble the chloride in many respects.

Among other stannous salts a sulphate, $SnSO_4$, is known. It is formed as a crystalline powder when a solution of stannous oxide in sulphuric acid is evaporated under the receiver of an air-pump. The feeble basic character of the stannous oxide is clearly evinced in the salt. It decomposes with extreme facility, when heated, into stannic oxide and sulphurous anhydride, but it easily forms double salts with the salts of the alkali metals.

In gaseous hydrochloric acid, stannous chloride, $SnCl_2,2H_2O$, forms a liquid having the composition $SnCl_2,HCl,3H_2O$ (sp. gr. 2·2, freezes at 27°), and a solid salt, $SnCl_2,H_2O$ (Engel).

coating ordinary tiles and similar earthenware objects with a layer of easily fusible glass or enamel. Acid solutions of stannic oxide treated with alkalis, and alkaline solutions when treated with acids, give a precipitate of stannic hydroxide, $Sn(OH)_4$, also known as stannic acid, which, when heated, gives up water and leaves the anhydride, SnO_2, which is insoluble in acids, clearly showing the feebleness of its basic character. When fused with alkali hydroxides (not with their carbonates or acid sulphates), an alkaline compound is obtained which is soluble in water. Stannic hydroxide, like the hydrates of silica, is a colloidal substance, and presents several different modifications, depending on the method of preparation, but having an identical composition; the various hydroxides have also a different appearance, and act differently with reagents. For instance, a distinction is made between ordinary stannic acid and metastannic acid. *Stannic acid* is produced by precipitation by soda or ammonia from a freshly-prepared solution of stannic chloride, $SnCl_4$, in water; on drying the precipitate thus obtained, a non-crystalline mass is formed, which is freely soluble in strong hydrochloric or nitric acids, and also in potassium and sodium hydroxides. This ordinary stannic acid may be still better obtained from sodium stannate by the action of acids. *Metastannic acid* is insoluble in sulphuric and nitric acids. It is obtained by treating tin with nitric acid, in the form of a heavy white powder; hydrochloric acid does not dissolve it immediately, but changes it to such an extent that, after pouring off the acid, water extracts the stannic chloride, $SnCl_4$, already formed. Dilute alkalis not only dissolve metastannic acid, but also transform it into salts, which, although slowly, yet completely dissolve in *pure water*, but are insoluble even in dilute alkali hydroxides. Dilute hydrochloric acid, especially when boiling, changes the ordinary hydrate into metastannic acid. On this depends, by the way, the formation of a white precipitate, stannic hydroxide, from solutions of stannous and stannic chlorides diluted with water. The stannic oxide first dissolved changes under the influence of hydrochloric acid into metastannic acid, which is insoluble in water in the presence of hydrochloric acid. Solutions of metastannic acid differ from such solutions of ordinary stannic acid, and in the presence of alkali they change into solutions of ordinary acid, so that metastannic acid principally corresponds with the acid compounds of stannic oxide, and ordinary stannic acid with the alkaline compounds.[40] Graham

[40] Fremy supposes the cause of the difference to consist in a difference of polymerisation, and considers that the ordinary acid corresponds with the oxide SnO_2, and the meta-acid with the oxide Sn_5O_{10}, but it is more probable that both are polymeric

obtained a soluble colloidal hydroxide; it is subject to the same transformations that are in general peculiar to colloids.

Stannic oxide shows the properties of a slightly energetic and intermediate oxide (like water, silica, &c.); that is to say, it forms saline compounds both with bases and with acids, but both are easily decomposed, and are but slightly stable. But still the acid character is more clearly developed than the basic, as in silica, germanic oxide, and lead dioxide. This determines the character of the compounds SnX_4.

Stannic chloride, $SnCl_4$ (also called tetrachloride of tin), is one of the compounds which most characteristically correspond with stannic oxide. It is obtained in an anhydrous condition by the direct action of chlorine on tin, and is then easily purified, because it is a liquid boiling at 114°, and therefore can be easily distilled. Its specific gravity is 2·28 (at 0°), and it fumes in the open air (spiritus fumans libarii); it shows the properties of a chloranhydride. Water, however, does not at first decompose it, but dissolves it, and on evaporation gives the crystallo-hydrate $SnCl_4,5H_2O$. If but little water be taken, crystals containing $SnCl_4,3H_2O$ are formed, which part with one-third of the water when placed under the receiver of the air-pump. A large quantity of water, however, especially when heated, causes a precipitate of metastannic acid.[41]

The alkali compounds of stannic oxide—that is, the compounds in

but in a different degree. Stannic acid with sodium carbonate gives a salt of the composition Na_2SnO_3. The same salt is also obtained by fusing metastannic acid with sodium hydroxide, whilst metastannic acid gives a salt, $Na_2SnO_3,4SnO_2$ (Fremy), when treated with a dilute solution of alkali; moreover, stannic acid is also soluble in the ordinary stannate, Na_2SnO_3 (Weber), so that both stannic acids (like both forms of silica) are capable of polymerisation, and probably only differ in its degree. In general, there is here a great resemblance to silica, and Graham obtained a solution of stannic acid by the direct dialysis of its alkaline solution. The main difference between these acids is that the meta-acid is soluble in hydrochloric acid, and gives a precipitate with sulphuric acid and stannous chloride, which do not precipitate the ordinary acid.

[41] The formation of the compound $SnCl_4,3H_2O$ is accompanied by so great a contraction that these crystals, although they contain water, are heavier than the anhydrous chloride $SnCl_4$. The meta-hydrated crystallo-hydrate absorbs dry hydrochloric acid, and gives a liquid of specific gravity 1·971, which at 0° yields crystals of the compound $SnCl_4,2HCl,6H_2O$ (it corresponds with the similar platinum compound), which melt at 20° into a liquid of specific gravity 1·925 (Engel).

Stannic chloride combines with ammonia ($SnCl_4,4NH_3$), hydrocyanic acid, phosphoretted hydrogen, phosphorus pentachloride ($SnCl_4PCl_5$), nitrous anhydride and its chloranhydride ($SnCl_4,N_2O_3$ and $SnCl_4,2NOCl$), and with metallic chlorides (for example, $K_2SnCl_6,(NH_4)_2SnCl_6$, &c.). In general, a highly-developed faculty for combination is observed in it. The development of this faculty in water, aluminium chloride, and other substances whose composition corresponds with the higher forms of combination of the elements, shows that they have affinities beyond those which determine the combination of their atoms. The peculiarity of these kinds of compounds is that they always combine

which it plays the part of an acid, corresponding in this way to the compounds of silica and other anhydrides of the composition RO_2—are very easily formed. They are distinguished by their great simplicity, and are used in the arts. Their composition in most cases corresponds with the formula SnM_2O_3—that is, $SnO(MO)_2$, similar to $CO(MO)_2$, where M=K, Na. Acids, even feeble acids like carbonic, decompose these salts, like the corresponding compounds of alumina or silica. In order to obtain *potassium stannate*, which crystallises in rhombohedra, and has the composition $SnK_2O_3,3H_2O$, potassium hydroxide (8 parts) is fused, and metastannic acid (3 parts) gradually added. A solution of the mass thus prepared, when evaporated in a desiccator, forms crystals of the above-mentioned composition. *Sodium stannate* has a similar composition. It is prepared in practice in large quantities by heating a solution of caustic soda with lead oxide and metallic tin. In this last case an alkaline solution of lead oxide is formed, and the tin acts on the solution in such a way as to reduce the lead to the metallic state, and itself passes into solution. This is very remarkable in this respect, that the lead displaces tin when in combination with acids, and the tin, on the contrary, displaces the lead from its alkali compounds. By dissolving the mass obtained in water, and then

with whole molecules capable of individual existence, and that such compounds resemble those with water of crystallisation in many respects.

Tin does not combine directly with iodine, but if its filings be heated in a closed tube with a solution of iodine in carbon bisulphide, it forms stannic iodide, SnI_4, in the form of red octahedra which fuse at 142° and volatilise at 295°. The fluorine compounds of tin have a special interest in the history of chemistry, because they give a series of double salts which are isomorphous with the salts of hydrofluosilicic acid, SiR_2F_6, and this fact served to confirm the formula SiO_2 for silica, as the formula SnO_2 was indubitable. However, *stannic fluoride*, SnF_4, is almost unknown in an isolated form, but its corresponding double salts are very easily formed by the action of hydrofluoric acid on alkaline solutions of stannic oxide; thus, for example, a crystalline salt of the composition SnK_2F_6,H_2O is obtained by dissolving stannic oxide in potassium hydroxide and then adding hydrofluoric acid to the solution. The barium salt, $SnBaF_6,3H_2O$, is sparingly soluble like its corresponding silicofluoride. The more soluble salt of strontium, $SnSrF_6,2H_2O$, crystallises very well, and is therefore more important for the purposes of research; it is isomorphous with the corresponding salt of silicon (and titanium); the magnesium salt contains $6H_2O$.

Stannic sulphide, SnS_2, is formed, as a yellow precipitate, by the action of sulphuretted hydrogen on acid solutions of stannic salts; it is easily soluble in ammonium and potassium sulphides, because it has an acid character, and then forms thiostannates (see Chapter XX.). In an anhydrous state it has the form of brilliant golden yellow plates, which may be obtained by heating a mixture of finely-divided tin, sulphur, and sal-ammoniac for a considerable time. It is sometimes used in this form under the name of mosaic gold, as a cheap substitute for gold-leaf in gilding wood articles. On ignition it parts with a portion of its sulphur, and is converted into stannous sulphide, SnS. It is soluble in caustic alkalis. Hydrochloric acid does not dissolve the anhydrous, crystalline compound, but the precipitated powdery sulphide is soluble in boiling strong hydrochloric acid, with the evolution of hydrogen sulphide.

adding alcohol, sodium stannate is precipitated, which may then be dissolved in water and purified by re-crystallisation. In this case it has the composition $SnNa_2O_3,3H_2O$ if separated from strong solutions, and $SnNa_2O_3,10H_2O$ when crystallised at a low temperature from dilute solutions. In the arts this salt is used as a mordant in dyeing operations, especially in the colouring of cotton fabrics. With a cold solution of sodium hydroxide metastannic acid forms a salt of the composition $(NaHO)_2,5SnO_2,3H_2O$, from which Frémy drew his conclusions concerning the polymerism of metastannic acid.

Tin occupies the same position amongst the analogues of silicon as cadmium and indium amongst the analogues of magnesium and aluminium respectively, and as in each of these cases the heavier analogues with a high atomic weight and a special combination of properties—namely, mercury and thallium—are known, so also for silicon we have *lead* as the heaviest analogue (Pb=206), with a series of both kindred and special properties. The principal peculiarity of the lead compounds consists in the higher type PbX_4, for instance, PbO_2, being in the chemical sense far less stable than the lower type PbX. The ordinary compounds of lead correspond with the latter, and in addition to this, PbO, although not particularly energetic, is still an evident base easily forming basic salts $PbX_2(PbO)_n$.

Lead is found in nature in considerable masses, in the form of galena, lead sulphide, PbS. The specific gravity of galena is 7·58, colour grey; it crystallises in the regular system, and has a fine metallic lustre. Both the native and artificial sulphides are insoluble in acids (hydrogen sulphide gives a black precipitate with the salts PbX_2).[42] When heated it melts, and in the open air is either totally or partially transformed into white lead sulphate, $PbSO_4$, as it also is by many oxidising agents (hydrogen peroxide, potassium nitrate). Lead sulphate is also insoluble in water,[43] and lead is but rarely met with in this form in nature. The chromates, vanadates, phosphates, and similar salts of lead are also rather rare. The carbonate $PbCO_3$ is sometimes found in large masses, especially in the Altai region. Lead sulphide is often worked for extracting the silver which it contains; but as the lead itself also finds manifold industrial appli-

[42] Lead sulphide in the presence of zinc and hydrochloric acid is completely reduced to metallic lead, all the sulphur being disengaged as hydrogen sulphide.

[43] Lead sulphate, $PbSO_4$, occurs in nature (*anglesite*) in transparent brilliant crystals which are isomorphous with barium sulphate, and have a specific gravity of 6·3. The same salt is formed on mixing sulphuric acid or its soluble salts with solutions of lead salts, as a heavy white precipitate, which is insoluble in water and acids, but dissolves in a solution of ammonium tartrate in the presence of an excess of ammonia, which serves to distinguish this salt from the similar salts of strontium and barium.

cations, this work is carried on on an exceedingly large scale. Two methods are principally applied. The first consists in decomposing the lead sulphide by heating it with cast iron. The iron takes up the sulphur from the lead, and forms easily-fusible iron sulphide, which does not mix with the heavier reduced lead. But another process is more frequently used, consisting in the following: the lead ore (it must be clean, that is, free from earthy matter, which may be easily removed by washing) is heated in a reverberatory furnace to a moderate temperature with a free access of air. During this operation part of the lead sulphide oxidises and forms lead sulphate, $PbSO_4$, and lead oxide. When the oxidation of part of the lead has been attained, it is necessary to shut off the air supply and increase the temperature, then the oxidised compounds of the lead enter into reaction with the remaining lead sulphide, with formation of sulphurous anhydride and metallic lead. At first from $PbS + O_3$, $PbO + SO_2$ are formed, and also from $PbS + O_4$ lead sulphate $PbSO_4$, and then PbO and $PbSO_4$ react with the remaining PbS, according to the equations $2PbO + PbS = 3Pb + SO_2$ and also $PbSO_4 + PbS = 2Pb + 2SO_2$.[44]

The appearance of lead is well known; its specific gravity is 11·3; the bluish colour and considerable metallic lustre of freshly-cut lead quickly disappears when exposed to the air, because it becomes coated with a layer—truly a very thin layer—of oxide and salts formed by the moisture and acids in the atmosphere. It melts at 326°, and crystallises in octahedra on cooling. Its softness is apparent from the flexibility of lead pipes and sheets, and also from the fact that it may be cut with a knife, and also that it leaves a grey streak when rubbed on paper. On account of its being so soft, lead naturally cannot be applied in many cases where most metals may be used; but, on the other hand, it is a metal which is not easily changed by chemical reagents, and as it is capable of being soldered and drawn into sheets, &c., lead is most valuable for many technical uses. Lead pipes are used for conveying water[45] and many other liquids, and sheet lead is used for lining all kinds of vessels containing liquids—for instance, acids, which act on other metals. This particularly refers to sulphuric and hydro-

[44] As lead is easily reduced from its ores, and the ore itself has a metallic appearance, it is not surprising that it was known to the ancients, and that its properties were familiar to the alchemists, who called it 'saturn.' Hence, metallic lead, reduced from its salts in solution by zinc, and which has the appearance of a tree-like mass of crystals, is called 'arbor saturni,' &c.

[45] Freshly laid new lead pipes contaminate the water with a certain amount of lead salts, proceeding from the presence of oxygen, carbonic acid, &c., in the water. But the lead pipes under the action of running water soon become coated with a film of salts—lead sulphate, carbonate, chloride, &c.—which are insoluble in water, and the water pipes then become harmless.

chloric acids, because at a low temperature they do not act on lead, and if they form lead sulphate, $PbSO_4$, and chloride, $PbCl_2$, these salts being insoluble in water and in acids, cover the lead and protect it from further corrosion.[46] All soluble preparations of lead are poisonous. At a white heat lead may be partially distilled; the vapours oxidise and burn. Lead may also be easily oxidised at low temperatures. Lead only decomposes water at a white heat, and does not liberate hydrogen from acids, with the exception only of very strong hydrochloric acid and then only when boiling. Sulphuric acid diluted with water does not act on it, or only acts very feebly at the surface; but strong sulphuric acid, when heated, is decomposed by it, with the evolution of sulphurous anhydride. The best solvent of lead is nitric acid, which transforms it into a soluble salt, $Pb(NO_3)_2$.

Although acids in this way directly have but little effect on lead, and this is one of its most important practical properties, *yet when air has free access, lead (like copper) very easily reacts with many acids*, even with those which are comparatively feeble. The action of acetic acid on lead in particular is clear and often applied in practice. If lead is plunged into acetic acid it does not change at all and does not pass into solution, but if part of the lead is immersed in the acid, and the other part remains in contact with the air, or if lead be merely covered with a thin layer of acetic acid, in such a way that the air is practically in contact with the metal, then it unites with the oxygen of the air to form oxide, which combines with the acetic acid and forms lead acetate, soluble in water. The formation of lead oxide may especially be observed from the fact that with a sufficient quantity of air, not only is the normal lead acetate formed, but also the basic salts.[47]

[46] Lead is not only used in the arts for drawing into tubes and sheets, for holding or conveying liquids, but also, owing to its considerable density, for being cast, when mixed with small quantities of other metals, into shot. A considerable amount is employed (together with mercury) in extracting gold and silver from poor ores, and in the manufacture of chemical reagents, and especially of lead chromate. *Lead chromate*, $PbCrO_4$, is distinguished for its brilliant yellow colour, owing to which it is employed in considerable quantities as a dye, mainly for dyeing cotton tissues yellow. It is formed on the tissue itself, by causing a soluble salt of lead to react on potassium chromate. Lead chromate is met with in nature as 'red lead ore.' It is insoluble in water and acetic acid, but it dissolves in aqueous potash. The so-called pewter vessels often consist of an alloy of 5 parts of tin and 1 part of lead, and solder is composed of 1 to 2 parts of tin with 1 part of lead. With respect to the alloys of lead and tin, Rudberg states that the alloy $PbSn_3$ stands out from the rest, because, according to his observations, the fall of temperature in the solidification of the alloy stops at 184°, which is the temperature at which this alloy solidifies. The composition of this alloy is nearly 37 p.c. of lead and 63 p.c. of tin.

[47] The normal lead acetate, known in trade as *sugar of lead*, owing to its having a sweetish taste, has the formula $Pb(C_2H_3O_2)_2,3H_2O$. This salt only crystallises from acid solutions. It is capable of dissolving a further quantity of lead oxide or of metallic lead in

When oxidising in the presence of air,[48] when heated or in the presence of an acid at the ordinary temperature, lead forms compounds of the type PbX_2. *Lead oxide*, PbO, known in industry as *litharge*, silberglätte (this name is due to the fact that silver is extracted from the lead ores of this kind) and massicot. If the lead is oxidised in air at a high temperature, the oxide which is formed fuses, and on cooling is easily obtained in fused masses which split up into scales of a yellowish colour, having a specific gravity of 9·3; in this form it bears the name of litharge. Litharge is principally used for making lead salts, and for the extraction of metallic lead, and also during the boiling of drying oils—for instance, linseed oil—that is, in the preparation of drying oils.[49] When oxidised carefully and slightly heated lead forms a powdery (not fused) oxide known under the name of *massicot*. It is best obtained by heating lead nitrate. Massicot is produced by heating lead

the presence of air. A basic salt of the composition $Pb(C_2H_3O_2)_2,PbH_2O_2$ is then formed, which is soluble in water and alcohol. As in this salt the number of atoms is even and the same as in the hydrate of acetic acid, $C_2H_4O_2,H_2O = C_2H_3(OH)_3$, it may be represented as this hydrate in which two of hydrogen are replaced by lead—that is, as $C_2H_3(OH)(O_2Pb)$. This basic salt is used in medicine as a remedy for inflammation, for bandaging wounds, &c., and also as a means for the manufacture of white lead. Other basic acetates of lead, containing a still greater amount of lead oxide, are known. According to the above representation of the composition of the preceding lead acetate, a basic salt of the composition $(C_2H_3)_2(O_2Pb)_3$ would be also possible, but what appear to be still more basic salts are known. As the character of a salt also depends on the property of the base from which it is formed, it would seem that lead forms a hydroxide of the composition HOPbOH, containing two water residues, one or both of which may be replaced by the acid residues. If both water residues are replaced, a normal salt XPbX is obtained, whilst if only one is replaced a basic salt, XPbOH, is formed. But lead does not only give this normal hydroxide, but also polyhydroxides, $Pb(OH),nPbO$, and if we may imagine that in these polyhydroxides there is a substitution of both the water residues by acid residues, then the power of lead for forming basic salts is explained by the properties of the base which enters into their composition.

[48] Few compounds are known of the lower type PbX, and still fewer of the intermediate type PbX_3. To the first type belongs the so-called lead suboxide, Pb_2O, obtained by the ignition of lead oxalate, C_2PbO_4, without access of air. It is a black powder, which easily breaks up under the action of acids, and even by the simple action of heat, into metallic lead and lead oxide. This is the character of all true suboxides. It does not give definite salts PbX, and therefore it cannot be regarded as a salt-forming oxide, neither can those forms of oxidation of lead which contain more oxygen than the oxide of lead, PbO, and less than the dioxide, PbO_2. As we shall see, at least two such compounds are formed. Thus, for example, an oxide having the composition Pb_2O_3 is known, but it is decomposed by the action of acids into lead oxide, which passes into solution, and lead dioxide, which remains behind. Such is red lead.

[49] In the boiling of drying oils, the lead oxide partially passes into solution, forming a saponified compound capable of attracting oxygen and solidifying into a tar-like mass, which forms the oil paint. Perhaps, however, glycerol partially acts in the process.

A mixture of very finely-divided litharge with glycerol (50 parts of litharge to 5 c.c. of anhydrous glycerol) forms a very quickly hardening (two minutes) cement, which is insoluble in water and oils, and is very useful in setting up chemical apparatus The hardening is based on the reaction of the lead oxide with glycerol (Moraffsky).

hydroxide. It has a yellow colour, and differs from litharge in the greater difficulty with which it forms lead salts with acids. Thus, for instance, when massicot is moistened with water it does not attract the carbonic acid of the air so easily as litharge does. It may, however, be imagined that the cause of the difference depends only on the formation of a portion of dioxide on the surface of the lead oxide, on which the acids do not act. In any case lead oxide is comparatively easily soluble in nitric and acetic acids. It is but slightly soluble in water, but communicates an alkaline reaction to it, naturally forming the hydroxide. But the remaining mass does not combine with the water. This hydroxide is obtained in the shape of a white precipitate by the action of a small quantity of an alkali hydroxide on a solution of a lead salt. An excess of alkali dissolves the hydroxide separated, which fact demonstrates the comparatively indistinct basic properties of lead oxide. The normal lead hydroxide, which should have the composition $Pb(OH)_2$, is unknown in a separate state, but it is known in combination with lead oxide as $Pb(OH)_2,2PbO$ or $Pb_3O_2(OH)_2$. The latter is obtained in the form of brilliant, white, octahedral crystals when basic lead acetate is mixed with ammonia and gently heated. The basic qualities of this hydroxide are shown distinctly by its absorbing the carbonic anhydride of the air. When an alkaline solution of the hydroxide is boiled, it deposits lead oxide in the form of a crystalline powder.

Lead oxide forms but few soluble salts—for instance, the nitrate and the acetate. The majority of its salts (sulphate, $PbSO_4$; carbonate, $PbCO_3$; iodide, PbI_2, &c.) are insoluble in water. These salts are colourless or light yellow if the acid is colourless. In lead oxide *the faculty of forming basic salts*, PbX_2nPbO or $PbX_2nPbH_2O_2$, is strongly developed. A similar property was observed in magnesium and also in the salts of mercury, but lead oxide forms basic salts with still greater facility, although double salts are in this case more rarely formed.[50]

[50] It is very instructive to observe that lead not only easily forms basic salts, but also salts containing several acid groups. Thus, for example, lead carbonate occurs in nature and forms compounds with lead chloride and sulphate. The first compound, known as *corneous lead, phosgenite*, has the composition $PbCO_3,PbCl_2$; it occurs in nature in bright cubical crystals, and is prepared artificially by simply boiling lead chloride with lead carbonate. A similar compound of normal salts, $PbSO_4,PbCO_3$, occurs in nature as *lanarkite* in monoclinic crystals. *Leadhillite* contains $PbSO_4,3PbCO_3$, and also occurs in yellowish, monoclinic, tabular crystals. We will turn our attention to these salts of lead, because it is very probable that their formation is allied to the formation of the basic salts, and the following considerations may guide to the explanation of the existence of one and the others. In describing silica we carefully developed the conception of polymerisation, which it is *indispensable to also recognise in the composition of many other oxides*. Thus it may be supposed that PbO_2 is a similar polymerised compound to SiO_2—*i.e.*, that the composition of lead peroxide will be Pb_nO_{2n}, because lead methyl,

Amongst the soluble lead salts, that best known and most often applied in practical chemistry is lead nitrate, obtained directly by dissolving lead or its oxide in nitric acid. The normal salt, $Pb(NO_3)_2$, crystallises in octahedra, dissolves in water, and has a specific gravity of 4·5. When a solution of this salt acts on white lead or is boiled with litharge, the basic salt, having a composition $Pb(OH)(NO_3)$, is formed in crystalline needles, sparingly soluble in cold water but easily dissolved in hot water, and therefore in many respects resembling lead chloride. When the nitrate is heated, either lead oxide is obtained or else the oxide in combination with peroxide.

Lead chloride, $PbCl_2$, is precipitated from the soluble salts of lead when a strong solution is treated with hydrochloric acid or metallic chloride. It is soluble in considerable quantities in hot water, and therefore if the solutions be dilute or hot, the precipitation of lead chloride does not occur, and if a hot solution be cooled, the salt separates in brilliant prismatic crystals. It fuses when heated (like silver chloride), but is insoluble in ammonia. This salt is rarely met with in nature, and when heated in air is capable of exchanging half the chlorine for oxygen, forming the basic salt or lead oxychloride,

$PbMe_4$, and lead ethyl, $PbEt_4$, are volatile compounds, whilst PbO_2 is non-volatile, and is very like silica in this respect, and not in the least like carbonic anhydride. As regards lead oxide, to it should still sooner be ascribed a polymeric structure, Pb_nO_n, all the more as it differs as little from lead dioxide in its physical properties as carbonic oxide does from carbonic anhydride, and as lead oxide is an unsaturated compound there is more likelihood for supposing it to be capable of intercombination (polymerisation) than lead dioxide. These considerations respecting the complexity of lead oxide could have no real meaning, and could not enter into the ranks of recognisable propositions, were it not for the existence of the above-mentioned basic and mixed salts. The oxide evidently corresponds with the composition Pb_nX_{2n}, and as, according to this representation, the number of X's in the salts of lead is considerable, it is obvious that they may be diverse. When a part of these X's is replaced by the water residue (OH) or by oxygen, $X_2=O$, and the other parts by an *acid residue*, X, then basic salts are obtained, but if a part of the X's is replaced by acid residues of one kind, and the other part by acid residues of another kind, then those mixed salts, about which we are now speaking, are formed. Thus, for example, we may suppose, for a comparison of the composition of the majority of the salts of lead, that $n=12$, and then the above-mentioned compounds will present themselves in the following form:—Lead oxide, $Pb_{12}O_{12}$, its crystalline hydrate, $Pb_{12}O_8(OH)_8$, lead chloride, $Pb_{12}Cl_{24}$, lead oxychloride, $Pb_{12}Cl_{12}O_6$, the other oxychloride, $Pb_{12}(OH)_6Cl_6O_6$, mendipite (*see* sequel), $Pb_{12}Cl_8O_8$, normal lead carbonate, $Pb_{12}(CO_3)_{12}$, crystalline basic salt, $Pb_{12}(OH)_6(CO_3)_6$, white lead, $Pb_{12}(CO_3)_8(HO)_8$, corneous lead, $Pb_{12}Cl_{12}(CO_3)_6$, lanarkite, $Pb_{12}(CO_3)_6(SO_4)_6$, leadhillite, $Pb_{12}(CO_3)_9(SO_4)_3$, &c. The number 12 here taken is only to avoid fractional quantities. Perhaps the polymerisation is much higher than this.

The conception of the polymerisation of oxides introduced by me in the first edition of this work (1869) is now beginning to be generally accepted. Thus Henry, Carnelley, Walker, and others see one proof of this in the fact that the hydrates of the majority of oxides only lose water little by little, and with difficulty towards the end, and also in the fact that oxides are less fusible and volatile than the corresponding chlorides, whilst oxygen is more difficultly liquefied and converted into a solid form than chlorine.

$PbCl_2PbO$, which may be obtained by fusing these two substances together. The reaction of lead chloride with water vapour leads to the same conclusion, showing the feeble basic character of lead and its power of entering into double decomposition with water:

$$2PbCl_2 + H_2O = PbCl_2,PbO + 2HCl.$$

When ammonia is added to an aqueous solution of lead chloride a white precipitate is formed, which parts with water on being heated, and has the composition $Pb(OH)Cl,PbO$. This compound is also formed by the action of metallic chlorides on other soluble basic salts of lead.[51]

Lead carbonate, or *white lead*, is the most extensively used basic lead salt. It has the valuable property of 'covering,' which only to a certain extent appertains to lead sulphate and other white powdery substances used as pigments. This faculty of 'covering' consists in the fact that a small quantity of white lead mixed with oil spreads uniformly, and if such a mixture be spread over a surface (for instance, of wood or metal) the surface is quickly covered—that is, it does not shine through the thin layer of superposed white lead; thus, for example, the grain of the wood remains invisible.[52] White lead, or *basic lead carbonate*, after being dried at 120°, has a composition $Pb(OH)_2,2PbCO_3$.[53] It may be obtained by adding a solution of sodium

[51] A similar basic salt having a white colour, and therefore used as a substitute for white lead, is also obtained by mixing a solution of basic lead acetate with a solution of lead chloride. Its formation is expressed by the equation: $2PbX(OH),PbO + PbCl_2 = 2Pb(OH)Cl,PbO + PbX_2$. Similar basic compounds of lead are met with in nature—for instance, *mendipite*, $PbCl,2PbO$, which appears in brilliant yellowish-white masses. The ignition of red lead with sal-ammoniac results in similar polybasic compounds of lead chloride, forming the *Cassel's*, or *mineral yellow* of the composition $PbCl_2nPbO$.

Lead iodide, PbI_2, is still less soluble than the chloride, and is therefore obtained by mixing potassium iodide with a solution of a lead salt. It separates as a yellow powder, which may be dissolved in boiling water, and on cooling separates in very brilliant crystalline scales of a golden yellow colour. The salts $PbBr_2$, PbF_2, $Pb(CN)_2$, $Pb_2Fe(CN)_6$ are also insoluble in water, and form white precipitates.

[52] It is remarkable that there exists a kind of peculiar attraction between boiled linseed oil and white lead, as is seen from the following experiments. White lead is triturated in water. Although it is heavier than water, it remains in suspension in it for some time and is thoroughly moistened by it, so that the trituration may be made perfect; boiled linseed oil is then added, and shaken up with it. A mixture of the oil and white lead is then found to settle at the bottom of the vessel. Although the oil is much lighter than the water it does not float on the top, but is retained by the white lead and sinks under the water together with it. There is not, however, any more perfect combination nor even any solution. If the resultant mass be then treated with ether or any other liquid capable of dissolving the oil, it passes into solution and leaves the white lead unaltered.

[53] It may be regarded as the type Pb_5X_6, in which X_4 is replaced by $(CO_3)_2$, or as a salt corresponding with the normal hydrate of carbonic acid $C(OH)_4$, in which three

carbonate to a solution of one of the basic salts of lead—for instance, the basic acetate—and likewise by treating this latter with carbonic acid. For this purpose the solution of basic acetate is poured into the vessel *f*; it is prepared in the vat A, containing litharge, into which the pump P delivers the solution of the acetate, which remains after the action of carbonic anhydride on the basic salt. In A a basic salt is formed having a composition approaching to $Pb_4(OH)_6(C_2H_3O_2)_2$; carbonic anhydride, $2CO_2$, is passed through this solution and precipitates

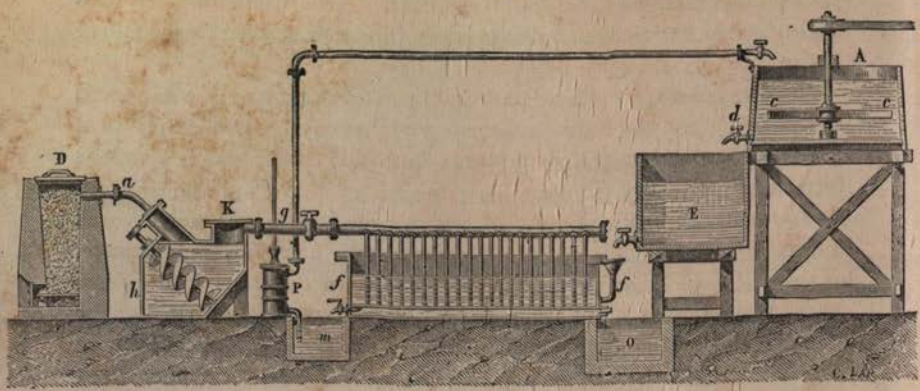

FIG. 82.—Manufacture of white lead.

white lead, $Pb_2(OH)_2(CO_3)_2$, and normal lead acetate, $Pb(C_2H_3O_2)_2$, remains in the solution, and is pumped back into the vat A containing lead oxide, where the normal salt is again (on being agitated) converted into the basic salt. This is run into the vessel E, and from thence into *f*. Into the latter carbonic anhydride is delivered from the generator D, from whence the gas is led by the pipe *g* through a series of small pipes which pass the gas through the solution of basic salt; white lead is

quarters of the hydrogen is replaced by lead. This mode of regarding the salt is really applicable in this case, because a salt is also known in which all the hydrogen of this hydrate of carbonic acid is replaced by lead—namely, the salt containing CO_4Pb_2. This salt is obtained as a white crystalline substance by the action of water and carbonic acid on lead. The normal salt, $PbCO_3$, occurs in nature under the name of white lead ore (sp. gr. 6·47), in crystals, isomorphous with aragonite, and is formed by the double decomposition of lead nitrate with sodium carbonate, as a white heavy precipitate. Thus both these salts resemble white lead, but the first-named salt is exclusively used in practice, owing to its being very conveniently prepared, and its being characterised by its great covering capacity, or 'body,' due to the fine grain of this salt.

One of the many methods by which white lead is prepared consists in mixing massicot with acetic acid or sugar of lead, and leaving the mixture exposed to air (and re-mixing from time to time), which contains carbonic acid, which is absorbed from the surface by the basic salt formed. After repeated mixings (with the addition of water), the entire mass is converted into white lead, which is thus obtained very finely divided.

precipitated by the action of the carbonic anhydride upon this solution, and the normal lead acetate remains in solution.

In order to mark the transition from lead oxide, PbO, into lead dioxide, PbO_2 (plumbic anhydride), it is necessary to direct our attention to the intermediate oxide, or *red lead*, Pb_3O_4.[54] In the arts it is used in considerable quantities, because it forms a fairly stable yellowish red paint used for colouring the resins (shellac, colophony, &c.) composing sealing wax. And it forms a very good cheap oil paint, used especially for painting metals, more particularly because drying oils—for instance, hemp seed, linseed oils—very quickly dry with red lead and with lead salts. Red lead is prepared by slightly heating massicot, for which purpose two-storied stoves are used. In the lower story the lead is turned into massicot, and in the higher one, having the lower temperature (about 300°), the massicot is transformed into red lead. Frémy and others showed the instability of red lead prepared by various methods, and its decomposition by acids, with formation of lead dioxide, which is insoluble in acids, and a solution of the salts of lead oxide. The artificial production (synthesis) of red lead by double decomposition was most important. For this purpose Frémy mixed alkaline solutions of potassium plumbate, K_2PbO_3 (prepared by dissolving the dioxide in fused potash), with an alkaline solution of lead oxide. In this way a yellow precipitate of minium hydrate is formed, which, when slightly heated, loses water and turns into bright red anhydrous minium, Pb_3O_4.

Minium is the first and most ordinary means of producing *lead dioxide*, or plumbic anhydride, PbO_2,[55] because when red lead is

[54] If lead hydroxide be dissolved in potash and sodium hypochlorite be added to the solution, then the oxygen of the latter acts on the dissolved lead oxide, and partially converts it into dioxide, so that the so-called lead sesquioxide is obtained; its empirical formula is Pb_2O_3. Probably it is nothing but a lead salt—*i.e.*, is referable to the type of dioxide of lead, or its hydroxide, $PbO(OH)_2$, in which two atoms of hydrogen are replaced by lead, $PbO(O_2Pb)$. We find a proof of this in the fact that the brown compound precipitated by the action of dilute acids—for example, nitric—splits up, even at the ordinary temperature, into insoluble lead dioxide and a solution of a lead salt. This compound evolves oxygen when it is heated. It dissolves in hydrochloric acid, forming a yellow liquid, which probably contains compounds of the composition $PbCl_2$ and $PbCl_4$, but even at the ordinary temperature this compound soon loses the excess of chlorine, and then only lead chloride, $PbCl_2$, remains. In order to see the relation between red lead and lead sesquioxide, it must be observed that they only differ by an extra quantity of lead oxide—that is, red lead is a basic salt of the preceding compound, and if the compound Pb_2O_3 may be regarded as PbO_3Pb, then red lead should be looked on as PbO_3Pb,PbO—that is, as basic lead plumbate.

[55] Lead dioxide is often called lead peroxide, but this name leads to error, because PbO_2 does not show the properties of true peroxides, like hydrogen or barium peroxides, but is endowed with acid properties—that is, it is able to form true salts with bases, which true peroxides do not do. Lead dioxide is a normal salt-forming compound of

treated with dilute nitric acid it gives up lead oxide and PbO_2 remains, on which dilute nitric acid does not act. The empirical composition of minium is Pb_3O_4, and therefore the action of nitric acid on it is expressed by the equation : $Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O$. This dioxide may be obtained by treating lead hydroxide suspended in water with a stream of chlorine. Here the chlorine takes up the hydrogen from the water, and the oxygen passes over to the lead oxide.[56] When a strong solution of lead nitrate is decomposed by the electric current, the appearance of crystalline lead dioxide is also observed upon the positive pole ; it is also found in nature in the form of a black crystalline substance having a specific gravity of 9·4. When artificially produced it is a fine dark powder, resisting the action of acids, but nevertheless, when treated with strong sulphuric acid, it evolves oxygen and forms lead sulphate, and with hydrochloric acid it evolves chlorine. The oxidising property of lead dioxide naturally

lead, as Bi_2O_5 is for bismuth, CeO_2 for cerium, and TeO_3 for tellurium, &c. They all evolve chlorine when treated with hydrochloric acid, whilst true peroxides form hydrogen peroxide. The true lead peroxide, if it were obtained, would probably have the composition Pb_2O_5, or, in combination with peroxide of hydrogen, $H_2Pb_2O_7 = H_2O_2 + Pb_2O_5$, judging from the peroxides corresponding with sulphuric, chromic, and other acids, as we shall afterwards consider.

As a proof of the fact, that the form PbO_2, or PbX_4, is the highest normal form of any combination of lead, it is most important to remark, that it might be expected that the action of lead chloride, $PbCl_2$, on zinc-ethyl, $ZnEt_2$, would result in the formation of zinc chloride, $ZnCl_2$, and lead-ethyl, $PbEt_2$, but in reality the reaction proceeds otherwise. Half of the lead is set free, and lead tetrethyl, $PbEt_4$, is formed as a colourless liquid, boiling at about 200° (Butleroff, Frankland, Buckton, Cahours, and others). The type PbX_4 is not only expressed in $PbEt_4$ and PbO_2, but also in PbF_4, obtained by Brauner.

Frémy obtained saline compounds of lead dioxide with bases. He obtained potassium plumbate in the following manner. Pure lead dioxide is placed in a silver crucible, and a strong solution of pure caustic potash is poured over it. The mixture is heated and small quantities are removed from time to time for testing, which consists in dissolving in a small quantity of water and decomposing the resultant solution with nitric acid. There is a certain moment during the heating when a considerable amount of insoluble lead dioxide is precipitated on the addition of the nitric acid; the solution then contains the salt in question, and the heating must be stopped, and a small amount of water added to dissolve the potassium plumbate formed. On cooling the salt separates in rather large crystals, which have the same composition as the stannate—that is, $PbO(KO)_2,3H_2O$. This analogy between lead dioxide and stannic oxide very clearly shows that the placing of lead in the same group as silicon and tin corresponds with the actual properties of this metal.

[56] According to Carnelley and Walker, the hydrate $(PbO_2)_5,H_2O$ is then formed; it loses water at 230°. The anhydrous dioxide remains unchanged to 280°, and is then converted into the sesquioxide, Pb_2O_3, which again loses oxygen at about 400°, and forms red lead, Pb_3O_4. Red lead also loses oxygen at about 550°, forming lead oxide, PbO, which fuses without change at about 600°, and remains constant as far as the limit of the observations made (about 800°).

The best method for preparing pure lead dioxide consists in mixing a hot solution of lead chloride with a solution of bleaching powder (Ferman).

depends on the facility of its transition into the more stable lead oxide, which is easily understood from the whole history of lead compounds. This oxidising property of the dioxide is particularly striking in the presence of alkalis. Thus under these conditions it transforms chromium oxide into chromic acid, whilst lead chromate, $PbCrO_4$, is formed, remaining, however, in solution, on account of its being soluble in caustic alkalis. The oxidising action of lead dioxide on sulphurous anhydride is most striking, as it immediately absorbs it, with formation of lead sulphate. This is accompanied by a change of colour and development of heat, $PbO_2+SO_2=PbSO_4$. When triturated with sulphur, lead peroxide causes flashes, because the sulphur burns at the expense of its oxygen.

Amongst the elements of the second and third groups it was observed that there were more basic elements in the even than in the uneven series. It is sufficient to remember calcium, strontium, and barium in the even and magnesium, zinc, and cadmium in the uneven series. In addition to this, as the atomic weight increases, in the same type of oxidation and group, the basic properties increase (the acid properties decrease), which is particularly striking in the even series—for example, in the second group, calcium, strontium, barium. The same also appears in the fourth and all the following groups. In the even series of the fourth group titanium, zirconium, cerium, and thorium are found. All their highest oxides, RO_2, even the lightest titanic oxide, TiO_2, have more highly developed basic properties than silica, SiO_2, and in addition to this the basic properties are more distinctly seen in zirconium dioxide, ZrO_2, than in titanic oxide, TiO_2, although the acid property of combining with bases still remains. In the heaviest oxides, cerium dioxide, CeO_2, and thorium dioxide, ThO_2, no acid properties are observed. Thorium dioxide, ThO_2, is purely a basic oxide, like cerium dioxide, CeO_2. In Chapter XVII. we already pointed out this higher oxide of cerium. As the above-mentioned elements are rather rare in nature, have but little practical application, and do not present any new forms of combination, it is unadvisable to dwell on them in this treatise.

Titanium is found in nature in the form of its anhydride or oxide, TiO_2, mixed with silicon in many minerals, but the oxide is also found separately (in débris and in seams) in the form of semi-metallic *rutile* (sp. gr. 4·2). Another titanic mineral is found as a mixture in many ores, known as *titanic iron ore* (in the Thuensky mountains of the southern Ural; it is known as *thuenite*), $FeTiO_3$. This is a salt of ferrous oxide and titanic anhydride. It crystallises in the rhombohedric system, has a metallic lustre, grey colour, sp. gr. 4·5. The third

mineral in which titanium is found in considerable quantities in nature is *sphene* or *titanite*, $CaTiSiO_5 = CaO,SiO_2,TiO_2$, sp. gr. 3·5, colour yellow, green, or such like, crystallises in tablets. The fourth, but rare, titanic mineral consists of *peroffskite*, calcium titanate, $CaTiO_3$; it forms blackish-grey or brown cubic crystals, sp. gr. 4·02, and occurs in the Ural and other localities. It may be prepared artificially by fusing sphene in an atmosphere of water vapour and carbonic anhydride. At the end of the last century Klaproth showed the distinction between titanic compounds and all others then known.[57]

[57] The compounds of titanium are generally obtained from rutile; the finely-ground ore is fused with a considerable amount of acid potassium sulphate, until the titanic anhydride, as a feeble base, passes into solution. After cooling, the resultant mass is ground up, dissolved in cold water, and treated with ammonium hydrosulphide; a black precipitate then separates out from the solution. This precipitate contains TiO_2 (as hydrate) and various metallic sulphides—for example, iron sulphide. It is first washed with water, and then with a solution of sulphurous anhydride until it becomes colourless. This is due to the iron sulphide contained in the precipitate, and rendering it black, being converted into dithionate by the action of the sulphurous acid. The titanic acid left behind is nearly pure. The considerable volatility of titanium chloride may also be taken advantage of in preparing the compounds of titanium from rutile. It is formed by heating a mixture of rutile and charcoal in dry chlorine; the distillate then contains *titanium chloride*, $TiCl_4$. It may be easily purified, owing to its having a constant boiling point of 136°. Its specific gravity is 1·76; it is a colourless liquid, which fumes in the air, and is perfectly soluble in water if it be not heated. If the action of titanic chloride on water be accompanied by heat, a large portion of titanic acid separates out from the solution and passes into metatitanic acid. A like decomposition of acid solutions of titanic acid is accomplished whenever they are heated, and especially in the presence of sulphuric acid, just as with metastannic acid, which titanic acid resembles in many respects. On igniting the titanic acid a colourless powder of the anhydride, TiO_2, is obtained. In this form it is no longer soluble in acids or alkalis, and only fuses in the oxy-hydrogen flame; but, like silica, it dissolves when fused with alkalis and their carbonates. But, as has been already mentioned, it also dissolves when fused with a considerable excess of acid potassium sulphate—that is, it then reacts as a feeble base. This shows the basic character of titanic anhydride; it has at once, although feebly developed, both basic and acid properties. The fused mass, obtained from titanic anhydride and alkali when treated with water, parts with its alkali, and a residue is obtained of a sparingly-soluble poly-titanate, $K_2TiO_3,nTiO_2$. The hydrate, which is precipitated by ammonia from the solutions obtained by the fusion of titanium compounds with acid potassium sulphate, when dried presents an amorphous mass of the composition $Ti(OH)_4$. But it loses water over sulphuric acids, and gradually passes into a hydrate of the composition $TiO(OH)_2$, and when heated it parts with a still larger proportion of water; at 100° the hydrate $Ti_2O_3(OH)_2$ being obtained, and at 300° the anhydride itself. The higher hydrate, $Ti(OH)_4$, is soluble in dilute acid, and the solution may be diluted with water; but on boiling the sulphuric acid solution (but not the solution in hydrochloric acid), all the titanic acid separates in a modified form, which is, however, not only insoluble in dilute acids, but even in strong sulphuric acid. This hydrate has the composition $Ti_2O_5(OH)_2$, but shows different properties from those of the hydrate of the same composition described above, and therefore we here again encounter a phenomenon of polymerisation similar to that which we saw with stannic acid. This modified hydrate is called *metatitanic acid*. It is most important to note the property of the ordinary gelatinous hydrate (that precipitated from acid solutions by ammonia) of dissolving in acids, all the more as silica does not show

The comparatively rare element *zirconium*, Zr = 90, is very similar to titanium, but shows a more basic character. It is rarer in nature than titanium, and is found principally in a mineral called *zircon*, $ZrSiO_4 = ZrO_2,SiO_2$, crystallising in square prisms, sp. gr. 4·5. It has considerable hardness and a characteristic brownish-yellow colour, and is occasionally found as transparent crystals, as a precious stone called hyacinth.[58] Metallic zirconium was obtained, by Berzelius and Troost,

this property. In this property a transition apparently appears between the cases of common solution (based on a capacity for unstable combination) and the case of the formation of a hydrosol (the solubility of germanium oxide, GeO_2, perhaps presents another similar instance). If titanium chloride be added drop by drop to a dilute solution of alcohol and hydrogen peroxide, and then ammonia be added to the resultant solution, there separates out a yellow precipitate of *titanium trioxide*, $TiO_3,3H_2O = Ti(OH)_6$, as Picini, Weller, and Classen showed. This substance evidently belongs to the category of true peroxides, which we shall consider in Chapter XX.

Titanium chloride absorbs ammonia and forms a compound, $TiCl_4,4NH_3$, as a red-brown powder which attracts moisture from the air, and when ignited forms *titanium nitride*, Ti_3N_4. Phosphuretted hydrogen, hydrocyanic acid, and many like compounds are also absorbed by titanium chloride, with the evolution of a considerable amount of heat. Thus, for example, a yellow crystalline powder of the composition $TiCl_4,2HCN$ is obtained by passing dry hydrocyanic acid vapour into cold titanium chloride. Titanium chloride combines in a similar manner with cyanogen chloride, phosphorus pentachloride, and phosphorus oxychloride, forming molecular compounds, for example, $TiCl_4,POCl_3$. This faculty for further combination probably stands in connection, on the one hand, with the capacity of titanium oxide to give polytitanates, $TiO(MO)_2,nTiO_2$; on the other hand, it corresponds with the kindred faculty of stannic chloride for the formation of poly-compounds (Note 14), and lastly it is probably related to the remarkable bearings of titanium towards nitrogen. Metallic titanium, obtained as a grey powder by reducing potassium titanofluoride, K_2TiF_6, with iron in a charcoal crucible, combines directly with nitrogen at a red heat. If titanic anhydride be ignited in a stream of ammonia, all the oxygen of the titanic oxide is disengaged, and the compound TiN_2 is formed as a dark violet substance having a copper-red lustre. A compound Ti_3N_6 is also known; it is obtained by igniting the compound Ti_3N_4 in a stream of hydrogen, and is of a golden-yellow colour with a metallic lustre. To this order of compounds there also belongs the well-known and chemically historical compound known as *titanium nitrocyanide*; its composition is Ti_3CN_4. This substance appears as infusible, sometimes well-formed, cubical crystals of sp. gr. 4·3, and having a red copper colour and metallic lustre; it is found in blast furnace slags. It is insoluble in acids, but is acted on by chlorine at a red heat, forming titanium chloride. It was at first regarded as metallic titanium; it is formed in the blast furnaces at the expense of those cyanogen compounds (potassium cyanide and others) which are always present, and at the expense of the titanium compounds which accompany the ores of iron. Wöhler, who investigated this compound, obtained it artificially by heating a mixture of titanic oxide with a small quantity of charcoal, in a stream of nitrogen, and thus proved the direct power for combination between nitrogen and titanium. When fused with caustic potash, all the nitrogen compounds of titanium evolve ammonia and form potassium titanate. Like metals they are able to reduce many oxides—for example, oxides of copper—at a red heat. Among the compounds of titanium, the crystalline compound Al_4Ti is also remarkable. It is obtained by directly dissolving titanium in fused aluminium; its specific gravity is 3·11. The crystals are very stable, and are only soluble in aqua regia and alkalis.

[58] The formula ZrO was first given to the oxide of zirconium as a base, in this case Zr = 45, whilst the present atomic weight is Zr = 90—that is, the formula of the oxide is now recognised as being ZrO_2. The reasons for ascribing this formula to the compounds

by the action of aluminium on potassium zirconofluoride in just the same way as silicon is prepared; it forms a crystalline powder, similar in appearance to graphite and antimony, but having a very considerable hardness, not much lustre, sp. gr. 4·15. In many respects it resembles silicon; it does not fuse when heated, and even oxidises with difficulty, but liberates hydrogen when fused with potash. When fused with silica it liberates silicon; hydrochloric and nitric acids act feebly on it, but aqua regia easily dissolves it. It is distinguished from silicon by the fact that hydrofluoric acid acts on it with great facility, even in the cold and when diluted, whilst on silicon this acid does not act at all.

Berzelius distinguished from zirconium the very similar element *thorium* (Th=232). It is very rarely met with, in *thorite* and

of zirconium are as follows: in the first place, the investigation of the crystalline forms of the zirconofluorides—for example, K_2ZrF_6, $MgZrF_6,5H_2O$—which proved to be analogous in composition and crystalline form with the corresponding compounds of titanium, tin, and silicon. In the second place, the specific heat of Zr is 0·067, which corresponds with the combining weight 90. The third and most important reason for doubling the combining weight of zirconium was given by Deville's determination of the vapour density of *zirconium chloride*, $ZrCl_4$. This substance is obtained by igniting zirconium oxide mixed with charcoal in a stream of dry chlorine, and is a colourless, saline substance which is easily volatile at 440°. Its density referred to air was found to be 8·15, that is 117 in relation to hydrogen, as it should be according to the above-cited molecular formula of this substance. It exhibits, however, in many respects a saline character, and that of an acid chloranhydride, for zirconium oxide itself presents very feebly developed acid properties but clearly marked basic properties. Thus zirconium chloride dissolves in water, and on evaporation the solution only partially disengages hydrochloric acid—like magnesium chloride, for example. Zirconium was discovered and characterised as an individual element by Klaproth.

Pure compounds of zirconium are generally prepared from zircon, which is finely ground, but as it is very hard it is first heated and thrown into cold water, by which means it is disintegrated. Zircon is decomposed or dissolved when fused with acid potassium sulphate, or still more easily when fused with acid potassium fluoride (a double soluble salt, K_2ZrF_6, is then formed); however, zirconium compounds are generally prepared from the powdered zircon by fusing it together with sodium carbonate and then boiling in water. An insoluble white residue is obtained consisting of a compound of the oxides of sodium and zirconium, which is then treated with hydrochloric acid and the solution evaporated to dryness. The silica is thus converted into an insoluble form, and zirconium chloride obtained in solution. Ammonia precipitates *zirconium hydroxide* from this solution, as a white gelatinous precipitate $ZrO(OH)_2$. When ignited this hydroxide loses water, and in so doing undergoes a spontaneous recalescence, and leaves a white, insoluble, and exceedingly hard mass of *zirconium oxide*, ZrO_2, having a specific gravity of 5·4. Owing to its infusibility, zirconium oxide is used as a substitute for lime and magnesia in the Drummond light. This oxide, in contradistinction to titanium oxide, is soluble even after prolonged ignition in strong hot sulphuric acid. The hydroxide is easily soluble in acids. The composition of the salts is ZrX_4, or $ZrOX_2$, or $ZrOX_2,ZrO_2$, just as with those of its analogues. But although zirconium oxide forms salts in the same way with acids, it also gives salts with bases. Thus it liberates carbonic anhydride when fused with sodium carbonate, forming the salts $Zr(NaO)_4$, $ZrO(NaO)_2$, &c. However, water destroys these salts and extracts the soda.

orangeite, $ThSiO_4,2H_2O$. The latter is isomorphous with zircon (sp. gr. 4·8).[59]

[59] Thorium has also been found in the form of oxide in certain pyrochlores, euxinites, and other rare minerals containing salts of niobium. The compounds of thorium are prepared by decomposing thorite or orangeite with strong sulphuric acid at its boiling-point; this renders the silica insoluble, and the thorium oxide passes into solution, when the residue is treated with cold water, after having been previously boiled with water (boiling water does not dissolve the oxide of thorium). Lead and other impurities are then separated by passing sulphuretted hydrogen through the solution, and then the thorium hydroxide is precipitated by ammonia. If this hydroxide be dissolved in the smallest possible amount of hydrochloric acid, and oxalic acid be then added, thorium oxalate is obtained as a white precipitate, which is insoluble in an excess of oxalic acid; this reaction is taken advantage of for separating this metal from many others. However, it resembles the cerite metals (Chapter XVII. Note 48) in this and many other respects. The thorium hydroxide is gelatinous; on ignition it leaves an infusible oxide, ThO_2, which, when fused with borax, gives crystals of the same form as stannic oxide or titanic anhydride; sp. gr., 9·7. But the basic properties are much more developed in thorium oxide than in the preceding oxides, and it does not even disengage carbonic acid when fused with sodium carbonate—that is, it is a much more energetic base than zirconium oxide. Thorium chloride is obtained as a distinctly crystalline sublimate when thorium oxide, mixed with charcoal, is ignited in a stream of dry chlorine. When heated with potassium, thorium chloride gives a metallic powder of thorium having a sp. gr. 11·1. It burns in air, and is but slightly soluble in dilute acids. The atomic weight of thorium was established by Chydenius and Delafontaine on the basis of the isomorphism of the double fluorides.

CHAPTER XIX

PHOSPHORUS AND THE OTHER ELEMENTS OF THE FIFTH GROUP

NITROGEN is the lightest and most widely distributed representative of the elements of the fifth group, which form a higher saline oxide of the form R_2O_5, and a hydrogen compound of the form RH_3. Phosphorus, arsenic, bismuth, and antimony belong to the uneven series of this group, and vanadium, niobium, and tantalum to the even series. The latter do not form compounds with hydrogen, like the elements of the even series in general (Chapter XV.); whilst phosphorus, arsenic, and antimony, on the other hand, are analogous to nitrogen, even in their property of forming RH_3. Phosphorus is the most widely distributed of these elements. There is hardly any mineral substance composing the mass of the earth's crust which does not contain some—it may be small—amount of phosphorus compounds in the form of the salts of phosphoric acid. The soil and earthy substances in general usually contain from one to ten parts of phosphoric acid in 10000 parts. This amount, which appears so small, has, however, a very important significance in nature. No plant can attain its natural growth if it be planted in an artificial soil completely free from phosphoric acid. Plants equally require the presence of potash, magnesia, lime, and ferric oxide, among basic, and of carbonic, sulphuric, nitric, and phosphoric anhydrides, among acid, oxides. In order to increase the fertility of a more or less poor soil, the above-named nutritive elements are introduced into it by means of fertilisers. Direct experiment has proved that these substances are inevitably necessary to plants, but that they must be all present simultaneously and in small quantities, and that an excess, like an insufficiency, of one of these elements is necessarily followed by a bad harvest, or the impossibility of a perfect growth, if the sum of all other conditions (light, heat, water, air) is normal. The phosphoric compounds of the soil accumulated by plants pass into the organism of animals, in which these substances are assimilated in many cases in large quantities. Thus

the chief component part of bones is calcium phosphate, $Ca_3P_2O_8$, on which the hardness of bones depends.[1]

Phosphorus was first extracted by Brand in 1669, by the ignition of evaporated urine. After the lapse of a century Scheele, who knew of the existence of a more abundant source of phosphorus in bones, pointed out the method which is now employed for the extraction of this element. Calcium phosphate in bones permeates a nitrogenous organic substance, which is called ossein, and forms a gelatin. When bones are treated exclusively for the extraction of phosphorus, neglecting the gelatin, they are burnt, in which case all the ossein is burnt away. When, however, it is desired to preserve the gelatin, the bones are immersed in cold dilute hydrochloric acid, which dissolves the calcium phosphate and leaves the gelatin untouched; calcium chloride and acid calcium phosphate, $CaH_4(PO_4)_2$, are then obtained in the solution. When the bones are directly burnt in an open fire, their mineral components only are left, as an ash, containing about 90 per cent. of calcium phosphate, $Ca_3(PO_4)_2$, mixed with a small amount of calcium carbonate and other salts. This mass is treated with sulphuric acid, and then the same substance is obtained in the solution as was obtained from the unburnt bones immersed in hydrochloric acid—*i.e.* the

[1] Dry bones contain about one-third of gelatinous matter and about two-thirds of ash, chiefly calcium phosphate.

The salts of phosphoric acid are also found in the mass of the earth as separate minerals; for example, the *apatites* contain this salt in a crystalline form, combined with calcium chloride or fluoride, $CaR_2,3Ca_3(PO_4)_2$, where R = F or Cl, sometimes in a state of isomorphous mixture. This mineral often crystallises in fine hexagonal prisms; sp. gr., 3·17 to 3·22. Vivianite is a hydrated ferrous phosphate, $Fe_3(PO_4)_2,8H_2O$. Phosphates of copper are frequently found in copper mines; for example, *tagilite*, $Cu_3(PO_4)_2,Cu(OH)_2,2H_2O$. Lead and aluminium form similar salts. They are nearly all insoluble in water. Sea and other waters always contain a small amount of phosphates. The ash of sea-plants, as well as of land-plants, always contains phosphates. Deposits of calcium phosphate are often met with; they are termed *phosphorites* and *osteolites*, and are composed of the fossil remains of the bones of animals; they are used for manure. Of the same nature are the so-called guano deposits from Baker's Island, and entire strata in Spain, France, and in the Governments of Orloff and Kursk in Russia. It is evident that if a soil destined for cultivation contain very little phosphoric acid, then the fertilisation by means of these minerals will be beneficial, but, naturally, only if the other elements necessary to plants be present in the soil.

Not unfrequently an untrue explanation of the conclusions made by Liebig with respect to the nourishment of plants by the component parts of the soil has led to a fervent and superfluous preaching in favour of manuring with phosphoric compounds. They are indispensable; but at the same time they are best and most economically applied together with other manures, whilst manuring with phosphoric compounds alone is not advantageous, and is therefore only necessary in very few cases—it cannot serve as a universal medicine for agriculture. It is not wise to introduce phosphoric manures in a given locality and under given conditions without making preliminary experiments.

acid calcium phosphate soluble in water, in which reaction naturally the chief part of the sulphuric acid is converted into calcium sulphate:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2.$$
$$Ca_3(PO_4)_2 + 4HCl = 2CaCl_2 + CaH_4(PO_4)_2.$$

On evaporating the solution, crystallisable acid calcium phosphate is obtained. The extraction of the phosphorus from this salt consists in *heating it with charcoal to a white heat.* When heated, the acid phosphate, $CaH_4(PO_4)_2$, first parts with water, and forms the metaphosphate, $Ca(PO_3)_2$, which, for the sake of simplicity, may be looked on, like the acid salt, as composed of pyrophosphate and phosphoric anhydride, $2Ca(PO_3)_2 = Ca_2P_2O_7 + P_2O_5$. The latter, with charcoal, gives phosphorus and carbonic oxide, $P_2O_5 + 5C = P_2 + 5CO$. So that, in reality, a somewhat complicated process takes place here, which, in ultimate products, will be as follows:

$$2CaH_4(PO_4)_2 + 5C = 4H_2O + Ca_2P_2O_7 + P_2 + 5CO.$$

After the steam has come over, phosphorus and carbonic oxide distil over from the retort, and calcium pyrophosphate remains behind.[2]

As phosphorus melts at about 40°, it condenses at the bottom of the receiver in a molten liquid mass, which is cast under water in tubes, and is sold in the form of sticks. This is common or *yellow phosphorus.* It is a transparent, waxy, yellowish substance, which is not brittle, almost insoluble in water, and easily undergoes change in its external appearance and properties, under the action of light, heat, and of various substances. It crystallises (by sublimation or from its solution in carbon bisulphide) in the regular system, and is especially characterised (in contradistinction to the other varieties) by its easy solubility in carbon bisulphide, and also partially in other oily liquids. In this it recalls common sulphur. Its specific gravity is 1·84. It fuses at 44°, and passes into vapour at 290°; it is easily inflammable, and must therefore be handled with great caution; careless rubbing is enough to cause phosphorus to ignite. Its application in the manufacture of matches is based on this. It emits light in the air owing to its oxidising, and is therefore kept under water (such water is phosphorescent in the dark, like phosphorus itself). It is also very easily oxidised by various oxidising agents, takes up the oxygen from many substances, and enters into direct combination with many metals and with sulphur, chlorine, &c., with development of a considerable amount of heat. It is very poisonous, although not soluble in water.

[2] By subjecting the pyrophosphate to the action of sulphuric or hydrochloric acid it is possible to obtain a fresh quantity of the acid salt from the residue, and in this manner

Besides this, there is a red variety of phosphorus, which differs considerably from the above. *Red phosphorus*, also called *amorphous phosphorus*, owing to its showing no sign of crystallisation, is partially formed when ordinary phosphorus remains long exposed to the action of light. It is also formed in many reactions; for example, when ordinary phosphorus combines with chlorine, bromine, iodine, or oxygen, a portion of it is converted into red phosphorus. Schrötter, in Vienna, investigated this variety of phosphorus, and pointed out by what methods it may be produced in considerable quantities. Red phosphorus is a powdery red-brown opaque substance of specific gravity 2·14. It does not combine so energetically with oxygen and other substances as yellow phosphorus, and evolves less heat in combining with them.[3] Common phosphorus easily oxidises in the air; red phos-

to extract all the phosphorus from the original normal salt $Ca_3(PO_4)_2$. It is usual to take burnt bones, but mineral phosphorites, osteolites, and apatites may also be employed as materials for the extraction of phosphorus. Its extraction for the manufacture of matches is everywhere extending, and in Russia, in the Urals, in the Government of Perm, it has attained such proportions that the district is able to supply other countries with phosphorus. A great many methods have been proposed for facilitating the extraction of phosphorus, but they none of them essentially differ from the usual one, because the problem is dependent on the liberation of phosphoric acid by the action of acids, and on its ultimate reduction by charcoal. Thus the calcium phosphate may be mixed directly with charcoal and quartz (silica), and phosphorus will be liberated on heating the mixture, because the silica displaces the phosphoric anhydride, which gives carbonic oxide and phosphorus with the charcoal. It has also been proposed to pass hydrochloric acid over an incandescent mixture of calcium phosphate and charcoal; the acid then acts just as the silica does, liberating phosphoric anhydride, which is reduced by the charcoal. It is necessary to prevent the access of air in the condensation of the vapours of phosphorus, because they take fire very easily; hence they are condensed under water by causing the gaseous products to pass through a vessel full of water. For this purpose the condenser shown in fig. 83 is usually employed.

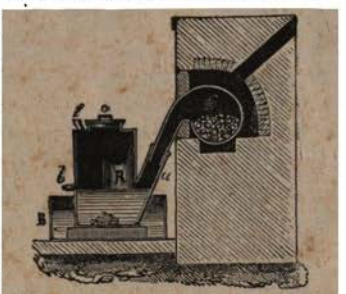

FIG. 83.—Preparation of phosphorus. The mixture is calcined in the retort *c*. The vapours of phosphorus pass through *a* into water without coming into contact with air. The phosphorus condenses in the water, and the gases accompanying it escape through *t*.

[3] The thermochemical determinations for phosphorus and its compounds date from the last century, when Lavoisier and Laplace burnt phosphorus in oxygen in an ice calorimeter. Andrews, Despretz, Favre, and others have studied the same subject. The most accurate and complete data are due to Thomsen. In order to give an idea of the indirect and complex methods by which the figures cited hereafter are obtained, it will be enough to point out that Thomsen employed the following method to determine the heat of combustion of yellow phosphorus. Phosphorus was oxidised in a calorimeter by iodic acid in the presence of water, and a mixture of phosphorous and phosphoric acids was thus formed (was not any hypophosphoric acid formed?—Salzer), and the iodic acid converted into hydriodic acid. It was first necessary to introduce two corrections into the calorimetric result obtained, one for the oxidation of the phosphorous into phosphoric acid, knowing their relative amounts by analysis, and the other for the deoxidation of

phorus does not oxidise at all at the ordinary temperature; hence it does not phosphoresce in the air, and may be very conveniently kept in the form of powder. It does not fuse at 44°. Having been converted into vapour at 290° or 300°, it, when slowly cooled, again passes into the ordinary variety. Red phosphorus is not soluble in carbon bisulphide and other oily liquids, which permits of its being freed from any admixture of the ordinary phosphorus. It is not poisonous. It is used in many cases for which the ordinary phosphorus is unsuitable or dangerous; for example, in the manufacture of matches, which are then no longer poisonous or inflammable by accidental friction, and therefore the red variety has now replaced the ordinary phosphorus.[4]

the iodic acid. The result then obtained expresses the conversion of phosphorous into hydrated phosphoric acid. This must be corrected for the heat of solution of the hydrate in water, and for the heat of combination of the anhydride with water, before we can obtain the heat evolved in the reaction of P_2 with O_5 in the proportion for the formation of P_2O_5. It is natural that with so complex a method there is a possibility of many small errors, and the resultant figures will only present a certain degree of accuracy after repeated corrections by various methods. Of such a kind are the following figures determined by Thomsen, which we express in thousands of calories:—$P_2+O_5=370$; $P_2+O_5+3H_2O=400$; P_2+O_5+ a mass of water $=405$. Hence we see that $P_2O_5+3H_2O=30$; $2PH_3O_4+$ a mass of water $=5$. Experiment further showed that crystallised PH_3O_4, in dissolving in water, evolves 2·7 thousand calories, and fused (39°) PH_3O_4 5·2 thousand calories, hence the heat of fusion of $H_3PO_4=2·5$ thousand calories. For phosphorous acid, H_3PO_3, Thomsen obtained $P_2+O_3+3H_2O=250$, and the solution of crystallised H_3PO_3 in water $=-0·13$, and of fused $H_3PO_3=+2·9$. For hypophosphorous acid, H_3PO_2, the heats of solution are nearly the same ($-0·17$ and $+2·1$), and the heat of formation $P_2+O+3H_2O=75$; hence its conversion into $2H_3PO_3$ evolves 175 thousand calories, and the conversion of $2H_3PO_3$ into $2H_3PO_4=150$ thousand calories. For the sake of convenience we will express the combination of chlorine with phosphorus, also according to Thomsen, per 2 atoms of phosphorus, $P_2+3Cl_2=151$, $P_2+5Cl_2=210$ thousand calories. In their reaction on a mass of water (with the formation of a solution), $2PCl_3=130$, $2PCl_5=247$, and $2POCl_3=142$ thousand calories.

Besides which we will cite the following data given by various observers: heat of fusion for P (that is, for 31 parts of phosphorus by weight) $-0·15$ thousand calories; the conversion of yellow into red phosphorus for P, from $+19$ to $+27$ thousand calories; $P+H_3=4·3$, $HI+PH_3=24$, $PH_3+HBr=22$ thousand calories.

[4] At the ordinary temperature (20° C.) phosphorus is not oxidised by pure oxygen; oxidation only takes place with a slight rise of temperature, or the dilution of the oxygen with other gases (especially nitrogen or hydrogen), or a direct decrease of pressure. Ordinary phosphorus takes fire at a temperature (60°) at which no other known substance will burn. Its application to the manufacture of matches is based on this property. The majority of *phosphorus matches* are composed of common phosphorus mixed with some oxidising substance which easily gives up oxygen, such as lead dioxide, potassium chlorate, nitre, &c. For this purpose common phosphorus is carefully triturated under warm water containing a little gum; lead dioxide, and potassium nitrate are then added to the resultant emulsion, and the match ends, previously coated with sulphur or paraffin, are dipped into this preparation. After this the matches are dipped into a solution of gum and shellac, in order to preserve the phosphorus from the action of the air. When such a match containing particles of yellow phosphorus is rubbed over a rough surface, it becomes (especially at the point of rupture of the brittle gummy coating) slightly heated, and this is sufficient for the phosphorus to take fire and burn at the

This red phosphorus is prepared by heating the ordinary phosphorus at 230° to 270°; it is evident that this must be done in an atmosphere incapable of supporting combustion—for example, in nitrogen, carbonic anhydride, steam, &c. On a large scale, ordinary phosphorus is placed in closed iron vessels,[5] fitted with a gas-conducting tube, and immersed in a bath of different proportions of tin and lead, by which means the temperature of 250° necessary for the conversion is easily attained. It is kept at this temperature for some time. The temperature is at first cautiously raised, and the air is thus partially expelled by the heat, and also by the evolution of steam (the phosphorus is damp when put in), whilst the remaining oxygen is also partially absorbed by the phosphorus, so that an atmosphere of nitrogen is produced in the iron vessel. Care must naturally be taken that no more air enters into the apparatus, and this is done by the aid of the gas-conducting tube, the end of which is immersed in mercury or other liquid. Red phosphorus enters into all the reactions proper to the common phosphorus, only with greater difficulty and more slowly;[6] and, as its vapour tension

expense of the oxygen of the other ingredients. In the so-called safety or Swedish matches (which are not poisonous, and do not take fire from accidental friction) a mixture of red phosphorus and glass is applied to the surface on which the matches are struck, and the matches themselves do not contain any phosphorus at all, but a mixture is taken of antimonious sulphide, Sb_2S_3 (because combustible substances act very well on it) and potassium chlorate (or other oxidising agents). The combustion, when once started by contact with the red phosphorus, proceeds by itself at the expense of the inflammatory and combustible elements contained in the tip of the match. The mixture applied on the match itself must not be liable to take fire from a blow or friction. In order to illustrate the easy inflammability of common (yellow) phosphorus, its solution in carbon bisulphide may be poured over paper; this solvent quickly evaporates, and the free phosphorus spread over a large surface takes fire spontaneously, notwithstanding the cooling effect produced by the evaporation of the bisulphide. The oxidation of phosphorus also proceeds at the expense of many other oxidising substances. Not only those oxidising agents like nitric, chromic, and other similar acids, but even alkalis, act as oxidising agents on phosphorus—that is, the latter acts as a reducing agent. Thus phosphorus is able to deoxidise many compounds—for example, it reduces copper from its salts. Phosphorus, when heated with sodium carbonate, reduces a portion of the carbon. If phosphorus be placed under water, slighted heated, and a current of oxygen be passed over it, it will burn under the water.

[5] Phosphorus only acts on iron at a red heat. The iron vessel is furnished with a safety valve.

[6] The specific heat of the yellow variety is 0·189—that is, greater than that of the red variety, which is 0·170. The sp. gr. of the yellow is 1·84, and of the red prepared at 260° 2·15, and of that prepared at 580° and above (this is 'metallic' phosphorus) = 2·34. At 230° the pressure of the vapour of ordinary phosphorus = 514 millimetres of mercury, and of the red = 0—that is to say, the red phosphorus does not form any vapour at this temperature; at 447° the vapour tension of ordinary phosphorus is at first = 5500 mm., but it gradually diminishes, whilst that of red phosphorus is equal to 1636 mm.

Hittorf, by heating the lower portion of a closed tube containing red phosphorus to 530° and the upper portion to 447°, obtained crystals of the so-called 'metallic' phosphorus at the upper extremity. This gives reason for thinking that the latter is crystallised

(volatility) is less than that of the yellow variety, one is led to think that a polymerisation proceeds in the passage of the yellow into the red modification, just as in the passage of cyanogen into paracyanogen, or of cyanic acid into cyanuric acid (Chapter IX. Vol. I. p. 398).

red phosphorus. But as the vapour tension (according to Hittorf, at 530° the vapour tension of yellow phosphorus = 8040 mm., of red = 6139 mm., and of metallic = 4130 mm.) and their reactions are different, *metallic phosphorus* may be regarded as a distinct variety. It is still less energetic in its chemical reaction than red phosphorus, and it is denser than the two preceding varieties: sp. gr. = 2·34. It does not oxidise in the air; is crystalline, and has a metallic lustre. It is obtained when ordinary phosphorus is heated with lead for several hours at 400° in a closed vessel, from which the air has been exhausted. The resultant mass is then treated with dilute nitric acid, which first dissolves the lead (phosphorus is electro-negative to lead, and does not, therefore, act on the nitric acid at first) and leaves brilliant rhombohedral crystals of phosphorus of a dark violet colour with a slight metallic lustre, which conduct an electric current incomparably better than the yellow variety; this also forms one of the signs of the metallic state of phosphorus.

The researches of Lemoine partially explained the passage of yellow (ordinary) phosphorus into its other varieties. He heated a closed glass globe containing ordinary and red phosphorus, in the vapour of sulphur (440°), and then determined the amount of the red and yellow varieties after various periods of time, by dissolving them in carbon bisulphide. It appeared that after the lapse of a certain time a mixture of definite and equal composition is obtained from both—that is, between the red and yellow varieties a state of equilibrium sets in, like that of dissociation, or that observed in double decompositions. But at the same time, the progress of the transformation appeared to be dependent on the relative quantity of phosphorus taken per given volume of the globe. Neglecting the latter, we will cite as an example the amounts of the red phosphorus transformed into the ordinary, and of the ordinary not converted into red, per 30 grams of red or yellow taken per litre of the capacity of the globe, heated to 440°. When red phosphorus was taken 4·75 grams of yellow phosphorus was formed after two hours, four grams after eight hours, three grams after twenty-four hours, and the last limit remained constant after further heating. When thirty grams of yellow phosphorus was taken, five grams remained unaltered after two hours, four grams after eight hours, and after twenty-four hours and more the same three grams as before. Troost and Hautefeuille showed that liquid phosphorus in general changes more easily into the red than does phosphorus vapour, which, however, is able, although slowly, to deposit red phosphorus.

The question presents itself as to whether phosphorus in a state of vapour is the ordinary or some other variety? Hittorf (1865) gave many data for the solution of this problem, among which there is no doubt that (as experimental figures show) the density of the vapour of phosphorus is always the same, although the vapour tension of the different varieties and their mixtures is very variable. This shows that the different varieties of phosphorus only appear in a liquid and solid state, which indeed expresses itself in the idea of polymerisation. Strictly speaking, the vapour of phosphorus is a particular state of this substance, and the molecular formula P_4 refers only to it, and not to any other definite state of phosphorus. But Raoult's method of solution (Vol. I. p. 90) showed that in a benzene solution the fall of the freezing point indicates a molecule P_4, perhaps mixed with P_2, for ordinary phosphorus, judging by the determination of Paterno and Nasini (1888), who for sulphur obtained by this method a molecular weight $= S_6$, as follows from the vapour density. Further research in this direction will perhaps show the possibility of finding the molecular weight of red phosphorus, if a means be discovered for dissolving it without converting it into the yellow variety. But as solution corresponds in many respects with evaporation (Chap I.), and as in evaporation one density is obtained answering to P_4, it may be that in this case Raoult's method will prove

The vapour of phosphorus is colourless; its density remains constant between 300° and 1000° (Dumas, 1833; Mitscherlich, Deville, and Troost, 1859, and others). The density with respect to air has been determined as from 4·3 to 4·5. Hence, referred to hydrogen, it is $4·4 \times 14·4 = 63$; and it corresponds with a molecular weight 124, or the molecule of phosphorus in a state of vapour contains P_4. The reader will remember that the molecule of nitrogen contains N_2, of sulphur S_6 and S_2, and of oxygen O_2 and O_3.

The chemical energy of phosphorus in a free state more nearly approaches that of sulphur than nitrogen. Phosphorus is combustible, inflames at 60°; but having parted with a portion of its energy in the act of combination, in the form of heat, it becomes analogous to nitrogen, so long as there be no question of its reduction back again into phosphorus. Nitric acid is easily reduced to nitrogen, whilst phosphoric acid is very much more difficultly reduced. All the compounds of phosphorus are less volatile than those of nitrogen. Nitric acid, HNO_3, is easily distilled; metaphosphoric acid, HPO_3, is, as is generally said, non-volatile; triethylamine, $N(C_2H_5)_3$, boils at 90°, and triethylphosphine, $P(C_2H_5)_3$, at 127°.

Phosphorus not only combines easily and directly with oxygen, but also with chlorine, bromine, iodine, sulphur, and with certain metals. So, for instance, when fused with sodium under naphtha, phosphorus gives the compound Na_3P_2. Zinc, absorbing the vapour of phosphorus, gives the phosphide Zn_3P_2 (sp. gr. 4·76); tin, SnP; copper, Cu_2P; even platinum combines with phosphorus (PtP_2, sp. gr. 8·77), and forms a brittle mass. Iron, when combined with even a small quantity of phosphorus, becomes brittle.[7] Some of these compounds of phosphorus are obtained by the action of phosphorus on the solutions of metallic

to be inapplicable to the accurate solution of the problem. One cannot but hope, however, that in the course of time new methods will be discovered, permitting the attainment of this purpose.

I think it will not be out of place to here turn the reader's attention to the fact that red phosphorus, which we must recognise as polymeric to the yellow, stands nearer to nitrogen, whose molecule is N_2, in its small inclination towards chemical reactions.

[7] The metallic compounds of phosphorus possess a great chemical interest, because they show a transition from metallic alloys (for instance, of Sb,As) to the sulphides, halogen salts, and oxides, and on the other hand to the nitrides. Although there are already many fragmentary data on the subject, still the interesting province of the metallic phosphides cannot yet be regarded as in any way generalised. The varied applications (phosphor-iron, phosphor-bronze, &c.), which the phosphides have recently acquired should give a most incentive reason for the complete and detailed study of this subject, which would, in my opinion, help to the explanation of chemical relations beginning with alloys (solutions) and ending with salts and the compounds of hydrogen (hydrides), because the phosphor-metals, as is proved by direct experiment, stand in the same relation to phosphuretted hydrogen as the sulphides do towards sulphuretted hydrogen, or as the metallic chlorides to hydrochloric acid.

salts, and by the ignition of metallic oxides in the vapour of phosphorus, or by heating mixtures of phosphates with charcoal and metals. Phosphides do not exhibit the external properties of salts, which are so clearly seen in the chlorides and still distinctly observable in the sulphides. *The phosphides of the metals* of the alkalis and of the alkaline earths are even immediately and very easily decomposed by water, which is found to be the case with only a very few sulphides, and still more rarely and indistinctly with the chlorides. This is the most remarkable property of the phosphides of the metals of the alkalis and alkaline earths. Take calcium phosphide, for example. Phosphorus is laid in a deep crucible, and covered with a clay plug, over which lime is strewn. At a red heat the vapours of phosphorus combine with the oxygen of the lime and form phosphoric anhydride, which forms a salt with another portion of the lime ; while the liberated calcium combines with the phosphorus and forms calcium phosphide. Its composition is not quite certain ; it may be CaP (corresponding with liquid phosphuretted hydrogen). This substance is remarkable for the following reaction : if we take water—or, better still, a dilute solution of hydrochloric acid—and throw calcium phosphide into it, then bubbles of gas are evolved, which take fire spontaneously in the air and form white rings. This is owing to the fact that the liquid hydrogen phosphide, PH_2, is first formed ; thus, $CaP+2HCl=CaCl_2+PH_2$, which, owing to its instability, very easily splits up into the solid phosphide, P_2H, and gaseous phosphide, PH_3 ; $5PH_2=P_2H+3PH_3$; the latter corresponds with ammonia. The mixture of the gaseous and liquid phosphides takes fire spontaneously in the air, forming phosphoric acid. The same hydrogen phosphides are formed when water acts on sodium phosphide (P_2Na_3). Hence we see that there are *three compounds of phosphorus with hydrogen* : (1) The first or solid yellow phosphide, P_2H (more probably P_4H_2), is obtained by the action of strong hydrochloric acid on sodium phosphide ; it takes fire when struck or at 175°. (2) The liquid, PH_2, or, more truly (molecule), P_2H_4, is a colourless liquid which takes fire spontaneously in the air, boils at 30°, is very unstable, and is easily decomposed (by light, hydrochloric acid) into the two other phosphides of hydrogen. It is prepared by passing the gases evolved by the action of water on calcium phosphide through a freezing mixture.[8] And, lastly, (3) gaseous hydrogen phosphide, *phosphine*, PH_3, which is distinguished as being the most stable. It is a colourless gas, which does not take fire in the air. It has an odour of garlic, and is very poisonous.

[8] The spontaneous inflammability of the hydride PH_2 in air is very remarkable, and it is particularly interesting that its analogues in composition $P(C_2H_5)_2$ (the formula must be doubled) and $Zn(C_2H_5)_2$ also take fire spontaneously in air.

It resembles ammonia in many of its properties. It is easily decomposed by heat, like ammonia, forming phosphorus and hydrogen; but it is very slightly soluble in water, and does not saturate acids, although it forms compounds with some of them which resemble ammonium salts in their form and properties. Among them the *compound with hydriodic acid*, PH_4I, analogous to ammonium iodide, is remarkable. This compound crystallises by sublimation in well-formed cubes, like sal-ammoniac, which it resembles in many respects. However, this compound does not enter into those reactions of double decomposition which are proper to sal-ammoniac, because its saline properties are very feebly developed. Phosphuretted hydrogen also combines, like ammonia, with certain chloranhydrides; but they are decomposed by water, with the evolution of phosphine. Ogier (1880) showed that hydrochloric acid also combines with phosphine under a pressure of 20 atmospheres at $+18°$, and under the ordinary pressure at $-35°$, forming the crystalline phosphonium chloride, PH_4Cl, corresponding to sal-ammoniac. Hydrobromic acid does the same with greater ease, and hydriodic acid with still greater facility, forming phosphonium iodide, PH_4I.[9]

Phosphuretted hydrogen, phosphine, PH_3, is generally prepared by the action of caustic potash on phosphorus.[10] Small pieces of phos-

[9] The periodic law and direct experiment (the molecular weight) show that phosphine is more simple than the solid hydride, just as methane, CH_4, is more simple than ethane, C_2H_6, whose empirical composition is CH_3. The formation of liquid phosphuretted hydrogen may be understood from the law of substitution. The univalent radicle of PH_3 is PH_2, and if it is combined with H in PH_3, it replaces H in liquid phosphuretted hydrogen, which thus gives P_2H_4. This substance corresponds with free amidogen (hydrazine), N_2H_4 (Vol. I. p. 287). Probably P_2H_4 is able to combine with HI, and perhaps also with 2HI, or other molecules—that is, to give a substance corresponding to phosphonium iodide.

Phosphonium iodide, PH_4I, may be prepared, according to Baeyer, in large quantities in the following manner:—100 parts of phosphorus are dissolved in dry carbon bisulphide in a tubulated retort: when the mixture has cooled, 175 parts of iodine are added little by little, and the carbon bisulphide is then distilled off, this being done towards the end of the operation in a current of dry carbonic anhydride at a moderate temperature. The neck of the retort is then connected with a wide glass tube, and the tubulure with a funnel furnished with a stop-cock, and containing 50 parts of water. This water is added drop by drop to the phosphorous iodide, and a violent reaction takes place, with the evolution of hydriodic acid and phosphonium iodide. The latter collects as crystals in the glass tube and the retort itself. It is purified by further distillations; more than 100 parts may be obtained. Baeyer expresses the reaction by the equation $P_2I+2H_2O=PH_4I+PO_2$; and the compound PO_2 may be represented as phosphorous phosphoric anhydride: $P_2O_5+P_2O_3=4PO_2$. As a better proportion we may take 400 grams of phosphorus, 680 grams of iodine, and 240 grams of water, and express the formation thus:—$13P+9I+21H_2O=3H_4P_2O_7+7PH_4I+2HI$ (Vol. I. p. 499).

Phosphonium iodide and even phosphine act as reducing agents on the solutions of many metallic salts. Cavazzi showed that with a solution of sulphurous anhydride, phosphine gives sulphur and phosphoric acid.

[10] The air must first be expelled from the flask by hydrogen, or some other gas which

phorus are dropped into a flask containing a strong solution of caustic potash and heated. Potassium hypophosphite, H_2KPO_2, is then obtained in solution; gaseous phosphuretted hydrogen is evolved:

$$P_4 + 3KHO + 3H_2O = 3(KH_2PO_2) + PH_3.$$

Liquid phosphuretted hydrogen is also formed, together with the phosphine, so that the gaseous product, on escaping from the water into the air, takes fire spontaneously, forming beautiful white rings of phosphoric acid. In this experiment, like that with calcium phosphide, it is the liquid, P_2H_4, that takes fire; but the phosphine set light to by it also burns, $PH_3 + O_4 = PH_3O_4$. The same phosphuretted hydrogen, PH_3, may be obtained pure, and not spontaneously combustible, by igniting the hydrates of phosphorous acid ($4PH_3O_3 = PH_3 + 3PH_3O_4$) and hypophosphorous acid ($2PH_3O_2 = PH_3 + PH_3O_4$); or, more simply, by the decomposition of calcium phosphide by hydrochloric acid, because then all the liquid phosphide, P_2H_4, is decomposed into non-volatile P_2H and gaseous PH_3.

Pure phosphine liquefies when cooled to $-90°$, boils at $-85°$, and solidifies at $-135°$ (Olszewski).

When phosphorus burns in an excess of *dry* oxygen, then only *phosphoric anhydride*, P_2O_5, is formed. It is prepared by throwing pieces of phosphorus through a wide tube, fixed into the upper neck of

will not support combustion, as otherwise an explosion might take place owing to the spontaneous inflammability of the phosphuretted hydrogen.

The following is another method by which gaseous phosphuretted hydrogen may be easily prepared: a mixture of one part of zinc dust to two parts of red phosphorus are put in an atmosphere of hydrogen or coal gas (it burns in air). Combination takes place, accompanied by a flash, and a green mass of zinc phosphide, Zn_3P_2, is formed, which gives phosphine with dilute sulphuric acid. The combustion of phosphuretted hydrogen in oxygen also takes place under water when the bubbles of both gases meet, and it is very brilliant. The phosphuretted hydrogen obtained by the action of phosphorus on caustic potash always contains free hydrogen, and often even the greater part of the gas evolved consists of hydrogen.

Pure phosphuretted hydrogen (not containing hydrogen or liquid or solid phosphides) is obtained by the action of a solution of potash on phosphonium iodide: $PH_4I + KHO = PH_3 + KI + H_2O$ (in just the same way as ammonia is from ammonium chloride). The reaction proceeds easily, and the purity of the gas is seen from the fact that it is entirely absorbed by bleaching powder and is not spontaneously inflammable. The vapours of bromine, nitric acid, &c., cause it to again acquire the property of inflaming in the air; that is, they partially decompose it, forming the liquid hydride, P_2H_4. Oppenheim showed that when red phosphorus is heated at 200° with hydrochloric acid in a closed tube it forms the compound $PCl_3(H_3PO_3)$ together with phosphine.

The analogy between phosphine and ammonia is particularly clearly shown in their hydrocarbon derivatives. Just as the compounds NH_2R, NHR_2, and NR_3, where R is CH_3, and other hydrocarbon radicles, correspond with NH_3, so also there are exactly corresponding compounds answering to PH_3. The study of these compounds belongs to organic chemistry.

a large glass globe, on to a cup suspended in the centre of the globe. These lumps are set light to by touching them with a hot wire, and the phosphorus burns into P_2O_5. The dry air necessary for its combustion is forced into the globe through a lateral neck, and the white flakes of phosphoric anhydride formed are carried by the current of air through a second lateral neck into a series of Woulfe's bottles, where they settle as friable white flakes. Phosphoric anhydride may also be formed by passing dry air through a solution of phosphorus in carbon bisulphide. All the materials for the preparation of this substance must be carefully dried, because it *combines* with great eagerness *with water*, at the same time developing a large amount of heat and forming metaphosphoric acid, HPO_3, from which the water cannot be separated by heat. Phosphoric anhydride is a colourless snow-like substance, which attracts moisture from the air with the utmost avidity. It fuses at a red heat, and then *volatilises*. Its affinity for water is so great that it takes it up from many bodies. Thus it converts sulphuric acid into sulphuric anhydride, and carbohydrates (wood, paper) are carbonised, and give up the elements of water to it when brought into contact with it.

When moist phosphorus slowly oxidises in the air, it not only forms phosphorous and phosphoric acids, but also *hypophosphoric acid*, $H_4P_2O_6$, which when in a dry state easily splits up at 60° into phosphorous and metaphosphoric acids ($H_4P_2O_6 = H_3PO_3 + HPO_3$), but differs from a mixture of these acids in that it forms well-characterised salts, of which the sodium salt, $H_2Na_2P_2O_6$, is but slightly soluble in water (the sodium salts of phosphoric and phosphorous acids are easily soluble), and that it does not act as a reducing agent, like mixtures containing phosphorous acid.[11] Thorpe, by oxidising phosphorus in

[11] Salzer proved the existence of hypophosphoric acid (it is also called subphosphoric acid), in which many chemists did not believe. Drawe (1888) investigated its salts. It may be obtained in a free state by the following method. The solution of acid produced by the slow oxidation of moist phosphorus is mixed with a solution (25 p.c.) of sodium acetate. A salt, $Na_2H_2P_2O_6,6H_2O$, crystallises out on cooling; it is soluble in 45 parts of water, and gives a precipitate of $Pb_2P_2O_6$ with lead salts ($Ag_4P_2O_6$ with salts of silver). The lead salt is decomposed by a current of hydrogen sulphide, when lead sulphide is precipitated, while the solution, evaporated under the receiver of an air-pump, gives crystals of $H_4P_2O_6,2H_2O$, which easily loses water and gives $H_4P_2O_6$. The salts, in which the H_4 is replaced by Ni_2, or $NiNa_2$, or $CdNa_2$, &c., are insoluble in water.

In order to see the relation between phosphoric acid and hypophosphoric acid which does not contain the elements of phosphorous acid (because it does not reduce either gold or mercury from their solutions), but which is nevertheless capable of being oxidised (for example, by potassium permanganate) into phosphoric acid, it is simplest to apply the law of substitution. This clearly indicates the relation between oxalic acid $(COOH)_2$ and carbonic acid, $OH(COOH)$, but the relation between the above acids is exactly the same if we express phosphoric acid as $OH(PO_2H_2)$, because in this case $P_2H_4O_6$, or $(PO_2H_2)_2$, will correspond with it just as oxalic does to carbonic acid. The relation

dry air, observed the formation of a volatile phosphorous oxide, P_2O_4, giving phosphoric and phosphorous acids with water, but which by its composition is the anhydride of hypophosphoric acid, $P_2O_4 = H_4P_2O_2 - 2H_2O$.

Judging by the common law of the formation of acids (Chapter XV.), the series of phosphorus compounds should include the following *ortho-acids* and their corresponding anhydrides, answering to phosphuretted hydrogen, H_3P :—

H_3PO_4, phosphoric acid, and	P_2O_5, anhydride,
H_3PO_3, phosphorous acid, and	P_2O_3, anhydride,
H_3PO_2, hypophosphorous acid, and	P_2O, anhydride.[12]

The last of these (the analogue of N_2O) is almost unknown, and the second is very little known. Phosphoric anhydride (P_2O_5) with a small quantity of water does not at first give orthophosphoric acid, PH_3O_4, but a compound P_2O_5,H_2O, or PHO_3, whose composition corresponds with that of nitric acid; this is *metaphosphoric acid.* Even with an excess of water, combining with phosphoric anhydride, this metaphosphoric acid, and not the ortho-, passes at first into solution. Metaphosphoric acid in solution only passes into orthophosphoric acid when the solution is heated or after the lapse of time.

Orthophosphoric acid [13] is obtained by oxidising phosphorus with nitric acid until the phosphorus entirely passes into solution and the lower oxides of nitrogen cease to be evolved. The reaction takes place best with dilute nitric acid, and when aided by heat. The resultant solution is evaporated to a syrup. If a weighed quantity of phosphorus

between hyposulphuric or dithionic acid, $(SO_2OH)_2$, and sulphuric acid, $OH(SO_2OH)$, is just the same, as we shall find in the following chapter. Dithionic acid corresponds with the anhydride S_2O_5, intermediate between SO_2 and SO_3; oxalic acid with C_2O_3, intermediate between CO and CO_2; hypophosphoric acid corresponds with the anhydride P_2O_4, also intermediate between P_2O_3 and P_2O_5.

[12] Besides the above enumerated hydrates, a compound, PH_3O, should correspond with PH_3. This hydrate, which is analogous to hydroxylamine, is not known in a free state, but it is known as triethylphosphine oxide, $P(C_2H_5)_3O$, which is obtained by the oxidation of triethylphosphine, $P(C_2H_5)_3$. It must be observed that there may also be lower oxides of phosphorus corresponding with PH_3, like N_2O and NO, and there are even indications of the formation of such compounds, but the data concerning them cannot be considered as firmly established.

[13] Phosphoric acid, being a soluble and non-volatile substance, cannot be prepared like hydrochloric and nitric acids by the action of sulphuric acid on the alkali phosphates, although it is partially liberated in the process. For this purpose the salts of barium or lead may be taken, because they give insoluble salts, thus $Ba_3(PO_4)_2 + 3H_2SO_4 = 3BaSO_4 + 2H_3PO_4$. Bone ash contains, besides calcium phosphate, sodium and magnesium phosphates, and fluorides and other salts, so that it cannot directly give a pure phosphoric acid.

(dried in a current of dry carbonic anhydride) be taken, then a crystalline mass of the acid can be obtained by evaporating the solution until it consists only of the quantity[14] of phosphoric acid corresponding with the amount of phosphorus taken (from 31 parts of P, 98 parts of solution). It fuses at +39°; sp. gr. of the liquid 1·88. Phosphorus pentachloride, PCl_5, and oxychloride, $POCl_3$ (see further on), give orthophosphoric acid and hydrochloric acid with water. The two other varieties of phosphoric acid, with which we shall presently become acquainted, give the same ortho-acid when in the presence of acids, with particular ease when boiled and more slowly in the cold. By itself orthophosphoric acid does not pass into the other varieties; it does not oxidise, and therefore forms the limiting and stable form. When heated to 300°, it loses water and passes into pyrophosphoric acid, $2H_3PO_4 = H_2O + H_4P_2O_7$, whilst at a red heat it loses twice as much water and is converted into metaphosphoric acid, $H_3PO_4 = H_2O + HPO_3$. In solution orthophosphoric acid exists as H_3PO_4, and not as pyro- or meta-phosphoric acids, because the solutions of these latter acids give different reactions: thus orthophosphoric acid does not precipitate albumin, does not give a precipitate with barium chloride, and forms a yellow precipitate of silver orthophosphate, Ag_3PO_4, with silver nitrate (in the presence of alkalis, but not otherwise); whilst a solution of pyrophosphoric acid, $H_4P_2O_7$, although it does not precipitate albumin or barium chloride, gives a white precipitate of silver pyrophosphate, $Ag_4P_2O_7$, with silver nitrate; and a solution of metaphosphoric acid, HPO_3, precipitates both albumin and barium chloride, and gives a white precipitate of silver metaphosphate, $AgPO_3$, with silver nitrate. These points of distinction were studied by Graham, and are exceedingly instructive. They show that the solution of a substance does not determine the maxima of chemical combination with water, that solutions may contain various degrees of combination with water, and that there is a clear difference between the water serving for solution and that entering into chemical combination. Graham's experiments also showed that the water whose removal or combination determines the conversion of ortho- into meta- and pyro-phosphoric acids differs distinctly from water of crystallisation, for he obtained the salts of ortho-, meta-, and pyrophosphoric acids with water of crystallisation, and they differed in their reactions, like the acids themselves, although their crystals contained water of crystallisation. This water was expelled with greater ease than the water of constitution of the hydrates in question.

[14] If this is not done the orthophosphoric acid, PH_3O_4, loses a portion of its water, and then, as with an excess of water, it does not crystallise.

Orthophosphoric acid has a pleasant acid taste and a distinctly acid reaction; it is used as a medicine, and is not poisonous (phosphorous acid is poisonous). Alkalis, like sodium, potassium, and ammonium hydroxides, saturate the acid properties of phosphoric acid when taken in the ratio $2NaHO : H_3PO_4$—that is, when salts of the composition HNa_2PO_4 are formed. When taken in the ratio $NaHO : H_3PO_4$, then a solution having an acid reaction is obtained, and when $3NaHO : H_3PO_4$—that is, when the salt Na_3PO_4 is formed—an alkaline reaction is obtained. Therefore many chemists (Berzelius) even regarded the salts of composition R_2HPO_4 as normal, and considered phosphoric acid to be bibasic. However, the salt Na_2HPO_4 also shows a feeble alkaline reaction, so that it is impossible to judge the characteristic peculiarities of acids by the reactions on litmus paper, as we already know from many examples. Orthophosphoric acid is tribasic, because it contains three equivalents of hydrogen replaceable by metals, forming salts, such as NaH_2PO_4, Na_2HPO_4, and Na_3PO_4. It is also tribasic, because with silver nitrate its soluble salts always give Ag_3PO_4,[15] a salt with three equivalents of silver, and because by double decomposition with barium chloride it forms a salt of the composition $Ba_3(PO_4)_2$, and silver and barium hardly ever give basic salts. With the metals of the alkalis, phosphoric acid forms soluble salts, but the normal salts of the metals of the alkaline earths, $R_3(PO_4)_2$ and even $R_2H_2(PO_4)_2$, are insoluble in water, but dissolve in feeble acids, like phosphoric and acetic, because they then form soluble acid salts, especially $RH_4(PO_4)_2$.[16]

[15] Silver orthophosphate, Ag_3PO_4, is yellow, sp. gr. 7·32, and insoluble in water. When heated it fuses like silver chloride, and if kept fused for some length of time it gives a white pyrophosphate (the decomposition which causes this is not known). It is soluble in aqueous solutions of phosphoric, nitric, and even acetic acids, of ammonia, and many of its salts. If silver nitrate acts on a dimetallic orthophosphate—for instance, Na_2HPO_4—it still gives Ag_3PO_4, nitric acid being disengaged: $Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3$. This is due to the property of silver of only giving normal salts by double decompositions in the presence of water. Of which fact the case in question is a proof, for when alcohol is added to silver orthophosphate, Ag_3PO_4, dissolved in syrupy phosphoric acid, it precipitates a white salt (the alcohol takes up the free phosphoric acid) having the composition Ag_2HPO_4, which is immediately decomposed by water into the normal salt and phosphoric acid.

[16] The researches of Thomsen showed that in very dilute aqueous solutions the majority of monobasic acids—nitric, acetic, hydrochloric, &c. (but hydrofluoric acid more and hydrocyanic less)—HR evolve the following amounts of heat (in thousands of calories) with caustic soda: $NaHO + 2HR = 14$; $NaHO + HR = 14$; $2NaHO + HR = 14$; that is, if n be a whole number $nNaHO + HR = 14$ and $NaHO + nHR = 14$. Hence reaction here only takes place between one molecule of NaHO and one molecule of acid, and the remaining quantity of acid or alkali does not enter into the reaction. In the case of bibasic acids, H_2R'' (sulphuric, dithionic, oxalic, sulphuretted hydrogen, &c.), $NaHO + 2H_2R'' = 14$; $NaHO + H_2R'' = 14$; $2NaHO + H_2R'' = 28$; $nNaHO + H_2R'' = 28$; that is, with an excess of acid ($NaHO + 2H'_2R''$) 14 thousand units of heat are developed, and with an excess of alkali 28. When phosphoric acid is taken (but not all tribasic acids—for instance, not citric) the

Phosphoric anhydride, or any of its hydrates, when ignited with an excess of sodium hydroxide, carbonate, &c., forms normal or *trisodium orthophosphate*, Na_3PO_4, but when a solution of sodium carbonate is decomposed by orthophosphoric acid, the salt Na_2HPO_4 only is formed; and when an excess of sodium chloride is ignited with orthophosphoric acid then hydrochloric acid is evolved, and the acid salt H_2NaPO_4 is alone formed. These facts clearly indicate the small energy of phosphoric acid with respect to the formation of the trimetallic salt, which is seen further from the fact that the salt Na_3PO_4 has an alkaline reaction, decomposes in the presence of water and carbonic acid, forming Na_2HPO_4, corrodes glass vessels in which it is boiled or evaporated, just like solutions of the alkalis, disengages, like them, ammonia from ammonium chloride, and crystallises from solutions, as $Na_3PO_4,12H_2O$, only in the presence of an excess of alkali. At 15° the crystals of this salt require five parts of water for solution; they fuse at 77°.

Disodium orthophosphate, or common sodium phosphate, Na_2HPO_4, is more stable both in solution and in the solid state. As it is used in

general character of the phenomenon is similar to the preceding, namely, $NaHO + 2H_3PO_4 = 14{\cdot}7$; $NaHO + H_3PO_4 = 14{\cdot}8$; $2NaHO + H_3PO_4 = 27{\cdot}1$; $3NaHO + H_3PO_4 = 34{\cdot}0$; $6NaHO + H_3PO_4 = 35{\cdot}3$; or, in general terms, $NaHO + nH_3PO_4 = 14$ (approximately), and $nNaHO + H_3PO_4 = 35$ and not 42, which shows a peculiarity of phosphoric acid. In the case of energetic acids, when one equivalent (23 grams) of sodium (in the form of hydroxide) replaces one equivalent (1 gram) of hydrogen (with the formation of water and in dilute solutions), 14000 heat units are evolved; and this is true for phosphoric acid when in H_3PO_4, Na or Na_2 replaces H or H_2, but when Na_3 replaces H_3 less heat is developed. This will be seen from the following arrangement based on the preceding figures: $H_3PO_4 + NaHO = 14{\cdot}8$; $NaH_2PO_4 + NaHO = 12{\cdot}3$; $Na_2HPO_4 + NaHO = 5{\cdot}9$; with $Na_3PO_4 + NaHO$, a very small amount of heat is evolved, as may be judged from the fact that $Na_3PO_4 + 3NaHO = 1{\cdot}3$, but still heat is evolved. One must suppose that in acting on phosphoric acid in the presence of a large quantity of water, a certain portion of the sodium hydroxide remains as alkali uncombined with the acid. Hence, on increasing the mass of the alkali, heat is still evolved, and a fresh interchange between Na and H takes place. Hence water shows a decomposing action on the alkali phosphates. When nH_3PO_4 is mixed with $nNaHO$ in a dilute solution, nNa_3PO_4 and $n3H_2O$ are not formed, but this reaction only takes place between $(n-m)H_3PO_4$ and $(n-m)3NaHO$, and hence the result will be a mixture of the solutions of $(n-m)Na_3PO_4, mH_3PO_4$ (or more probably of acid salts), mNaHO and OH_2, and therefore the solution of Na_3PO_4 has an alkaline reaction. The same decomposing action of water is seen, but to a less extent, with Na_2HPO_4, as may be judged both from the reactions of this salt and from the amount of heat developed by NaH_2PO_4 with NaHO. Such an explanation is in accordance with many facts concerning the decomposition of salts by water already known to us, and shows that in the presence of a mass of water thermochemical data cannot be the means of discovering the nature of acids, but rather the means for demonstrating the effects of water on salts, if the data obtained by this means be compared with other data relative to the salts. Recent researches made by Berthelot and Louguinine have confirmed the above deductions made by me in the first edition (1871) of this work. Now views of this nature are already somewhat generally accepted, although they are not sufficiently strictly applied in other cases.

medicine and in dyeing, it is prepared in considerable quantities, most frequently from the impure phosphoric acid obtained by the action of sulphuric acid on bone ash. The solution thus formed—which contains, besides phosphoric and sulphuric acids, salts of sodium, calcium, and magnesium—is heated, and sodium carbonate added so long as carbonic anhydride is disengaged. A precipitate is formed containing the insoluble salts of magnesium and calcium, while the solution contains sodium phosphate, Na_2HPO_4, with a small quantity of other salts, from which it may be easily purified by crystallisation. At the ordinary temperature its solutions, especially in the presence of a small amount of sodium carbonate, give finely-formed inclined prismatic crystals, $Na_2HPO_4,12H_2O$;[17] when the crystallisation takes place at above 30° they only contain $7H_2O$. The former crystals even lose a portion of their water of crystallisation at the ordinary temperature (the salt effloresces), and form the second salt with $7H_2O$; whilst under the receiver of an air-pump and over sulphuric acid they also part with this water. When ignited they lose the last molecule of water of constitution, and give sodium pyrophosphate, $Na_4P_2O_7$. The crystals of $Na_2HPO_4,12H_2O$ have a sp. gr. of 1·53, and dissolve in 4·9 parts of water at 16°. The solution has a feeble alkaline reaction, and absorbs carbonic anhydride.

Monosodium orthophosphate, NaH_2PO_4, crystallises with one equivalent of water ; its solution has an acid reaction. At 100° the salt only loses this water of crystallisation, and at 200° to 240° it parts with all its water, forming the metaphosphate $NaPO_3$. It is prepared from ordinary sodium phosphate by adding phosphoric acid until the solution does not give a precipitate with barium chloride, and then evaporating and crystallising the solution. The solution of this salt does not absorb carbonic anhydride, and does not give a precipitate with salts of calcium, barium, &c.[18]

[17] $Na_2HPO_4,12H_2O$ has a sp. gr. 1·53. Poggiale determined the solubility in 100 parts of water (1) of the anhydrous ortho-salt Na_2HPO_4, and (2) of the corresponding pyro-salt $Na_4P_2O_7$:—

	0°	20°	40°	80°	100°
I.	1·5	11·1	30·9	81	108
II.	3·2	6·2	13·5	30	40

At temperatures of 20° to 100° the ortho-salt is so very much less soluble that this difference alone already indicates the deeply-seated alteration in constitution which takes place in the passage from the ortho- to the pyro-salts.

[18] The ammonium *orthophosphates* resemble the sodium salts in many respects, but the instability of the di- and tri-metallic salts is seen in them still more clearly than in the sodium salts; thus $(NH_4)_3PO_4$, and even $(NH_4)_2HPO_4$ lose ammonia in the air (especially when heated, even in solutions); $NH_4H_2PO_4$ alone does not disengage ammonia and has an acid reaction. The crystals of the first salt contain $3H_2O$, and are only

As a hydrate, orthophosphoric acid should be expressed, after the fashion of other hydrates, as containing three water residues (hydroxyl

formed in the presence of an excess of ammonia; both the others are anhydrous, and may be obtained like the sodium salts. When ignited these salts leave metaphosphoric acid behind; for example, $(NH_4)_2HPO_4 = 2NH_3 = H_2O + HPO_3$. Ammonia also enters into the composition of many double phosphates. Ammonium sodium orthophosphate, or simply phosphate, $NH_4NaHPO_4,4H_2O$, crystallises in large transparent crystals from a mixture of the solutions of disodium phosphate and ammonium chloride (in which case sodium chloride is obtained in the mother liquid), or, better still, from a solution of monosodium phosphate saturated with ammonia. It is also formed from the phosphates in urine when it ferments. This salt is frequently used in testing metallic compounds by the blow-pipe, because when ignited it leaves a vitreous metaphosphate, $NaPO_3$, which, like borax, dissolves metallic oxides, forming characteristic tinted glasses.

When a solution of trisodium phosphate is added to a solution of a magnesium salt it gives a white precipitate of the normal orthophosphate $Mg_2(PO_4)_2,7H_2O$. If the trisodium salt be replaced by the ordinary salt, Na_2HPO_4, a precipitate is also formed, and $MgHPO_4,7H_2O$ is obtained. It might be thought that the normal salt $Mg_3(PO_4)_2$ would be precipitated if disodium phosphate was added to ammonia and a salt of magnesium, but in reality *ammonium magnesium orthophosphate*, $MgNH_4PO_4,6H_2O$, is precipitated as a crystalline powder, which loses ammonia and water when ignited, and gives a pyrophosphate, $Mg_2P_2O_7$. This salt occurs in nature as the mineral struvite, and in various products of the changes of animal matter. If we consider that the above salt parts with ammonia with difficulty, and that the corresponding salt of sodium is not formed under the same conditions ($MgNaPO_4,9H_2O$ is obtained by the action of magnesia on disodium phosphate), if we turn our attention to the fact that the salts of calcium and barium do not form double salts as easily as magnesium, and if we recollect that the salts of magnesium in general easily form double ammonium salts, then we are led to think that this salt is not really a normal, but an acid salt, corresponding with Na_2HPO_4, in which Na_2 is replaced by the group NH_3Mg, equivalent to two of sodium.

The common normal *calcium phosphate*, $Ca_3(PO_4)_2$, occurs in minerals, in animals, especially in bones, and also probably in plants, although the ash of many portions of plants, as a rule, contains less lime than the formation of the normal salt requires. Thus 100 parts of the ash (from 5000 parts of grain) of rye grain contain 47·5 of phosphoric anhydride and only 2·7 of lime, and even the ash of all the rye (including straw) contains twice as much phosphoric anhydride as lime, and the normal salt contains almost equal weights of these substances. Only the ash of grasses, and especially of clover, and of trees, contain in the majority of cases more lime than is required for the formation of $Ca_3P_2O_8$. This salt, which is insoluble in water, dissolves even in such feeble acids as acetic and sulphurous, and even in water containing carbonic acid. The latter fact is of immense importance in nature, because by its means rain water is able to transfer the calcium phosphates in the soil into solutions which are absorbed by plants. The solubility of the normal salt in acids takes place in virtue of the formation of an acid salt, which is evident from the quantity of acid required for its solution, and more especially from the fact that the acid solutions when evaporated give crystalline scales of the acid calcium phosphate, $CaH_4(PO_4)_2$, soluble in water. This solubility of the acid salt forms the basis of the treatment by acids of bones, phosphorites, guano, and other natural products containing the normal salt and employed for fertilising the soil. The perfect decomposition requires at least $2H_2SO_4$ to $Ca_3(PO_4)_2$, but in reality less is taken, so that only a portion of the normal salt is converted into the acid salt. Hydrochloric acid is sometimes used. (In practice such mixtures are known as *superphosphates*.) Certain experiments, however, show that a careful grinding, the presence of organic, and especially of nitrogenous, substances, and the porous structure of calcium phosphates (for example, as in burnt bones), render the treatment of phosphoric manures by acids superfluous—that is, the crop is not bettered by it.

groups), *i.e.* as $PO(OH)_3$. This method of expression indicates that the type PX_5, seen in PH_4I, is here preserved, with the substitution of X_2 by oxygen and X_3 by three hydroxyl groups. The same type appears in $POCl_3$, PCl_5, PF_5, &c. And if we recognise phosphoric acid as $PO(OH)_3$, we should expect to find three anhydrides corresponding with it: (1) $[PO(OH)_2]_2O$, in which two of the three hydroxyls are preserved; this is pyrophosphoric acid, $H_4P_2O_7$. (2) $PO(OH)O$, where only one hydroxyl is preserved. This is metaphosphoric acid. (3) $(PO)_2O_3$ or P_2O_5, that is, perfect phosphoric anhydride. Therefore, *pyro- and meta-phosphoric acids are imperfect anhydrides* (or anhydro-acids) *of orthophosphoric acid.*[19]

Pyrophosphoric acid, $H_4P_2O_7$, is formed by heating orthophosphoric acid to 300°, which then loses water. Its normal salts are formed by igniting the dimetallic salts of orthophosphoric acid of the types HM_2PO_4. Thus from the disodium salt we obtain sodium pyrophosphate $Na_4P_2O_7$ (it crystallises from water with $10H_2O$, is very stable, fuses when heated, has an alkaline reaction, and does not form ortho- salts when its solution is boiled): and from the monosodium salt NaH_2PO_4 the acid salt $Na_2H_2P_2O_7$ (easily soluble in water) is formed; this has an acid reaction, and when ignited further gives the meta-salt.[20]

[19] In this sense the ortho-acid itself might be regarded as an anhydro-acid, counting $P(HO)_5$ as the perfect hydrate, if PH_5 existed; but as in general the normal hydrates correspond with the existing hydrogen compounds with the addition of up to 4 atoms of oxygen, therefore PH_3O_4 is the normal acid, just as SH_2O_4 and $ClHO_4$; but NHO_3, CH_2O_3 are meta-acids, or higher normal acids (NH_3O_4 and CH_4O_4) with the loss of a molecule of water.

In order to see the relation between the ortho-, pyro-, and meta-phosphoric acids, the first thing to remark is that in them the anhydride P_2O_5 is combined with 3, 2, and 1 molecule of water. But such an empirical relation does not express the entire reality, because the pyrophosphoric acid is not obtained (?) in the conversion of the meta- into the ortho-acid; for instance, when the former is obtained from the anhydride and converted into the ortho-acid by heating its solution. The intimate relation between the ortho- and meta-acids is better expressed by the ordinary formulæ, which show that the ortho-acid, H_3PO_3, and the meta-acid, HPO_3, contain one atom of phosphorus, whilst the molecule of the pyro-acid, $H_4P_2O_7$, has two. Still, even this expression of the composition of these acids does not correspond with facts, because all the data, hereafter considered, respecting metaphosphoric acid show (Note 21) that its molecule is much more complex, is polymerised, and contains at least $H_3P_3O_9$; the like cannot be said as to nitric acid. The explanation of the problems which here present themselves can, it seems to me, be only looked for after a detailed study of the phenomena of the polymerisations of mineral substances, and of those complex acids, such as phosphomolybdic, which we shall hereafter (Chapter XXI.) describe. A similar instance is exhibited in the solubility of hydrate of silica (produced by the action of silicon fluoride on water) in fused metaphosphoric acid, with the formation, on cooling, of an octahedral compound (sp. gr., 3·1) containing SiO_2,P_2O_5.

[20] The method of preparation of the acid itself consists in converting the sodium salt, $Na_4P_2O_7$, by double decomposition with water and a salt of lead, into insoluble lead

Metaphosphoric acid, HPO_3 (the analogue of nitric acid), is formed by the ignition of the pyro- and ortho-acids (or, better, of their ammonium salts), as a glassy, hygroscopic, fused mass (glacial phosphoric acid, *acidum phosphoricum glaciale*), soluble in water and volatilising without decomposition. It is also formed in the first slow action of cold water on the anhydride, but metaphosphoric acid gradually changes into the ortho-acid when its solution is boiled, or when it is kept for any length of time, especially in the presence of acids.[21]

pyrophosphate, $Pb_2P_2O_7$, which is then shaken up in water and decomposed by sulphuretted hydrogen; lead sulphide is thus precipitated, and pyrophosphoric acid remains in solution. This solution cannot be heated, or the pyro-acid will pass into the ortho-, but must be evaporated under the receiver of an air-pump. It concentrates to a syrup and crystallises, and when ignited in this form it loses water, and forms metaphosphoric acid. It resembles orthophosphoric acid in many respects; its salts with the alkalis are also soluble, and the others insoluble in water but soluble in acids. When heated in solution with acid it gives orthophosphoric acid, as well as when fused with an excess of alkali.

I may here remark that Witt heated ammonium chloride with phosphoric acid (hydrochloric acid was evolved), ignited the residue to drive off ammonia, and obtained pyrophosphoric acid in the residue.

[21] As when using phenolphthalein as an indicator in neutralising by an alkali metaphosphoric acid is monobasic, and orthophosphoric acid is bibasic, it is possible by means of this difference to follow the transition of meta- into ortho-phosphoric acid. Sabatier (1888) carried on an investigation of this nature, and found that the rate of transformation is dependent on the temperature, and is subject to the general laws of the rate of chemical transformations, to whose consideration we shall return in the following chapter.

Metaphosphoric acid has a particular interest in respect to the variations to which its salts are subject. The metaphosphates are formed by the ignition of the acid orthophosphates, MH_2PO_4, or MNH_4HPO_4, or of the acid pyrophosphates, $M_2H_2P_2O_7$, or $M_2(NH_4)_2P_2O_7$, water and ammonia being given off in the process. The properties of the metaphosphates, which have a similar composition to nitrates—for instance, $NaPO_3$, or $Ba(PO_3)_2$—vary according to the duration of the ignition to which the ortho-, or pyrophosphates from which they are prepared have been subjected. When the salts NaH_2PO_4 or NH_4NaHPO_4 are strongly ignited, a salt $NaPO_3$ is formed, which deliquesces in the air, and gives a gelatinous precipitate with salts of the alkaline earths. But, as Graham (in 1830–40) and many others, especially Fleitmann and Henneberg (*in* 1840–50), observed, under other conditions the salts of the same composition acquire other properties. The above chemists recognise five polymeric forms of metaphosphates, $(HPO_3)_n$, where n varies from 1 to 6. We will mention certain of these varieties, following the nomenclature and researches of Fleitmann.

Monometaphosphoric acid. The salts are distinguished for their insolubility in water; even the salts $NaPO_3$, KPO_3, are insoluble. They are obtained by igniting the monometallic orthophosphates—for example, RH_2PO_4—up to the temperature at which all water is evolved (316°), but not to fusion. No double salts are known.

Dimetaphosphoric acid, on the contrary, easily forms double salts—for example, $KNaP_2O_6$, and also the copper potassium salt, &c. The copper salt is obtained by evaporating a solution of copper oxide in orthophosphoric acid. A blue ortho-salt, $CuHRO_4$, first separates from the solution, then a light-blue pyro-salt, $Cu_2P_2O_7$; and above 350°, when metaphosphoric acid itself begins to volatilise, the dimetaphosphate, CuP_2O_6, is formed. The residue is washed with water, and decomposed with a hot solution of sodium sulphide, and then the sodium salt, $Na_2P_2O_6$, is obtained in solution. This salt, when evaporated with alcohol, gives crystals containing 2 mol. H_2O, which, however, retain their solubility (in 7 parts of water) after the water is driven off at 100°. When fused, these

In order to see the relation between phosphoric acid and the lower acids of phosphorus, it is simplest to imagine the substitution of hydroxyl by hydrogen. Then from orthophosphoric acid, $PO(OH)_3$, we shall obtain phosphorous acid, $POH(OH)_2$ and hypophosphorous acid, $POH(OH)$; and, furthermore, phosphorous acid should be bibasic if orthophosphoric acid was tribasic, and hypophosphorous acid should be monobasic. This conclusion is indeed true, and this shows that all the acids of phosphorus may be referred to one common type PX_5, whose representatives are PH_4I and PCl_5.

Phosphorous acid, PH_3O_3, is generally obtained from phosphorus trichloride, PCl_3, by the action of water: $PCl_3 + 3H_2O = 3HCl + PH_3O_3$. Both acids formed are soluble in water, but are easily separated, because hydrochloric acid is volatile whilst phosphorous acid volatilises with difficulty, and if a small amount of water be originally taken the hydrochloric acid nearly all passes off directly. Concentrated solutions of phosphorous acid give crystals of H_3PO_3, which fuse at 70°, attract moisture from the air, and deliquesce when ignited, giving phosphine and phosphoric acid,[22] and are oxidised into orthophosphoric acid by

crystals give a deliquescent salt (hexa-metaphosphate). The solution of the salt has a neutral reaction, which only after prolonged boiling becomes acid, owing to the formation of orthophosphate, NaH_2PO_4. The soluble salts of dimetaphosphoric acid give the insoluble silver salt, $Ag_2P_2O_6$, with silver nitrate, and a precipitate of $BaP_2O_6,2H_2O$ with barium chloride.

Trimetaphosphoric acid is obtained as the sodium salt $Na_3P_3O_9$ when any other metaphosphate of sodium is fused and *slowly* cooled, then dissolved in a slight excess of warm water, and the resultant solution evaporated. The crystals contain 6 mol. H_2O, and dissolve in four parts of water. An acid reaction is only obtained, as with the preceding salt, after prolonged boiling with water. The acid is a true analogue of nitric acid, because *all its metallic salts are soluble*.

Hexametaphosphoric acid. Fleitmann so named the ordinary metaphosphoric acid (glacial) which attracts moisture. The deliquescent sodium salt is obtained, like the trimetaphosphate, only by *rapid* cooling. It is also formed by fusing silver oxide with an excess of phosphoric acid. The sodium salt is soluble in water, and gives viscous, elastic precipitates with salts of Ba, Ca, and Mg.

Jawein and Thillot (1889), who investigated the sodium salts of metaphosphoric acid by Raoult's method, came to the conclusion that the salts of di- and tri-metaphosphoric acid behave in such a manner that their molecule must be represented as non-polymerised $NaPO_3$, whilst those of hexametaphosphoric acid behave as $(NaPO_3)_4$. At all events, the series of salts which Fleitmann and Henneberg regard as monometaphosphates are, in my opinion, most probably the most polymerised, because they are insoluble.

[22] Phosphorous acid, when subjected to the action of nascent hydrogen (zinc and sulphuric acid), evolves phosphine, and when boiled with an excess of alkali it evolves hydrogen ($PH_3O_3 + 3KHO = PK_3O_4 + 2H_2O + H_2$); owing to its liability to oxidation, it is a reducing agent—for instance, it reduces cupric chloride to cuprous chloride, and precipitates silver from the nitrate and mercury from its salts. According to Amat, phosphorous acid easily gives corresponding salts with NH_3 and $2NH_3$, and forms a pyrophosphorous acid, $P_2H_4O_5$.

These reactions are perhaps connected with the fact that in this acid one atom of hydrogen should be considered as in the same condition as in phosphuretted hydrogen,

many oxidising agents. In its salts only two hydrogen atoms are replaced by metals (Würtz); the salts of the alkaline metals are soluble, and give precipitates with salts of the majority of other metals.

The monobasic *hypophosphorous acid*, PH_3O_2, gives salts PH_2O_2Na, $(PH_2O_2)_2Ba$, &c.; the two remaining atoms of hydrogen (which exist in the same form as in phosphine, PH_3) are not replaceable by metals, and this determines the property of these salts of evolving phosphuretted hydrogen when heated (especially with alkalis). In acting on substances liable to reduction it is this hydrogen which acts, and, for example, *reduces* gold and mercury from the solutions of their salts, or converts cupric into cuprous salts. In all these instances the hypophosphorous acid is converted in phosphoric acid. Under the action of zinc and sulphuric acid it gives phosphine, PH_3. Nevertheless, neither hypophosphorous acid nor its dry salts absorb oxygen from the air. The salts of hypophosphorous acid are more soluble than those of the preceding acids of phosphorus. Thus the sodium salt $PNaH_2O_2$ does not give a precipitate with barium chloride, and the salts of calcium, barium, and many other metals are soluble.[23] The hypophosphites are prepared by boiling an alkali with phosphorus so long as phosphuretted hydrogen is evolved. The acid itself is obtained from barium hypophosphite (prepared in the same manner by boiling phosphorus in baryta water), by decomposing its solution with sulphuric acid. By concentration of the solution of hypophosphorous acid (it must not be heated above 130°, at which temperature it decomposes) a syrup is formed which is able to crystallise. In the

which is expressed by the formula $PHO(OH)_2$, if we represent it as PH_4X, with the substitution of two of the hydrogen atoms by oxygen and of HX by two of hydroxyl. The direct passage of phosphorous chloride into phosphorous acid would, however, indicate that all the three atoms of hydrogen in it occur in the form of hydroxyl, because no difference is known between the three atoms of chlorine in PCl_3—they all react alike, as a rule. However, Menshutkin, by acting on alcohol, C_2H_5OH, with phosphorous chloride, obtained hydrochloric acid and a substance $P(C_2H_5O)Cl_2$, and from it by the action of bromine he obtained ethyl bromide, C_2H_5Br, and a compound $PBrOCl_2$, which proves, to a certain extent, the existence of a difference between the three atoms of chlorine in phosphorous chloride.

If we turn our attention to the formation of phosphine by the ignition of phosphorous acid, then we see that $4PH_3O_3$ only evolve 3H in the form of PH_5, and therefore the residue—that is, $3PH_3O_4$—will still contain one hydrogen of the same nature as in phosphine, because in $4PH_3O_5$ we should recognise four such hydrogens as in phosphine. We arrive at the same conclusion by examining the decomposition of hypophosphorous acid, $2PH_3O_2 = PH_3 + PH_3O_4$. In the two molecules of the monobasic hypophosphorous acid taken, there are only two atoms of hydrogen replaceable by metals, whilst in the molecule of the resultant phosphoric acid there are three. Perhaps relations of this nature determine the relative stability of the di-metallic salts of orthophosphoric acid.

[23] Calcium hypophosphite is used in medicine. According to Cavazzi, a mixture of sodium hypophosphite, NaH_2PO_2, and sodium nitrate explodes violently.

solid state hypophosphorous acid fuses at +17°, and has the properties of a clearly-defined acid.

The types PX_4 and PX_5, which are evident for the hydrogen and oxygen compounds of phosphorus, are most clearly seen in its halogen compounds,[24] to the consideration of which we will proceed, fixing our attention more especially on the chlorine compounds, as being the most important from the historical, theoretical, and practical point of view.

Phosphorus burns in chlorine, forming phosphorous chloride, PCl_3, and with an excess of chlorine, phosphoric chloride, PCl_5. The oxychloride, $POCl_3$, as the simplest chloranhydride according to the type PX_5, and also phosphoric chloride, correspond with orthophosphoric acid, $PO(OH)_3$, and phosphorous chloride, PCl_3, corresponds with phosphorous acid and the type PX_3. Phosphoric oxychloride, $POCl_3$, is a colourless liquid, boiling at 110°. Phosphorus trichloride is also a colourless liquid, boiling at 73°,[25] whilst phosphoric chloride is a solid

[24] Fluorine and bromine give PX_3 and PX_5 like chlorine. With respect to iodine PI_5 is, in a chemical sense, a very unstable substance. *Phosphorus tri-iodide* is easily formed (from yellow or red phosphorus and iodine in the requisite proportions). It is a red crystalline substance, fuses at 55°, is easily decomposed by water, forming phosphorous and hydriodic acids, and when heated it evolves iodine vapours and forms phosphorus di-iodide, PI_2. This substance may be obtained in the same manner as the preceding by taking a smaller proportion of iodine (8 parts of iodine to 1 part of water, whilst the tri-iodide requires 12·3); it also forms red crystals, which melt at 110°. When decomposed by water it not only gives phosphorous and hydriodic acids, but also phosphine and a yellow substance (a lower oxide of phosphorus). In its composition di-iodide of phosphorus corresponds with liquid phosphuretted hydrogen, PH_2, and probably its molecular weight is much higher: P_2I_4 or P_3I_6, &c. As the iodine compounds of phosphorus give hydriodic and phosphorous acids with water, and as both these substances are reducing agents in the presence of water (and hydrates), iodide of phosphorus also acts as a reducing agent.

[25] In a liquid state the density of phosphorous chloride at 10° = 1·597, and therefore its molecular volume = 137·5/1·597 = 86·0, and that of phosphorus oxychloride is equal to 153·5/1·693 = 90·7; hence the addition of oxygen has produced considerable increase in volume, just as in the conversion of sulphur dichloride, SCl_2, into sulphuryl chloride, $SOCl_2$, the volume varies from 64 to 71. It is the same with the boiling points; phosphorus trichloride boils at 70°, the oxychloride at 100°, sulphur dichloride at 64°, and sulphuryl chloride at 78—that is, the addition of oxygen raises the boiling points.

The vapour density of phosphorus trichloride and oxychloride corresponds with their formulæ—namely, is equal to half the molecular weight referred to hydrogen. In reality, the observed vapour density of phosphorus trichloride with respect to air = 4·8 (Cahours) —that is, 69·1 referred to hydrogen, whilst according to its formula it should be 68·7; in the case of phosphorus oxychloride, the observed vapour density referred to air = 5·4 (Würtz), and 5·3 (Cahours at 275°), hence the mean referred to hydrogen = 77, whilst according to the formula it should be 72·7. Hence the formulæ of phosphorus trichloride and oxychloride correspond with two volumes, as do those of all whole molecules. But it is not so with phosphorus pentachloride. Cahours showed that the vapour density of phosphorus pentachloride referred to air = 3·65, to hydrogen = 52·6, whilst according to the formula PCl_5 it should be = 104·2. Hence this formula corresponds with four, and not with two, molecules. This shows that the vapour of phosphoric chloride contains two and not one molecule, that in a state of vapour it splits up, like sal-ammoniac (Vol. I.

yellowish substance, infusible but straightway volatilising at about 168°. They are all heavier than water, and form types of the *chloranhydrides* or chlorine compounds of the non-metallic elements whose hydrates are acids, just as NaCl or $BaCl_2$ are types of the saline metals.

If a piece of phosphorus be dropped into a flask containing chlorine, it burns when touched with a red-hot wire, and combines with the chlorine. If the phosphorus be in excess, then liquid *phosphorus trichloride*, PCl_3, is always formed, but if the chlorine be in excess then the solid pentachloride is obtained. The trichloride is generally prepared in the following manner. Dry chlorine (passed through a series of Woulfe's bottles containing sulphuric acid) is led into a retort containing sand and phosphorus. The retort is heated, and the phosphorus melts into a liquid, spreads through the sand, and gradually forms the trichloride, which distils over into a receiver, where it condenses. *Phosphoric chloride*, or *phosphorus pentachloride*, PCl_5, is prepared by passing dry chlorine into a vessel containing phosphorus trichloride (purified by distillation). Phosphorous chloride combines directly with oxygen, but more rapidly with ozone, or with the oxygen of potassium chlorate ($3PCl_3 + KClO_3 = 3POCl_3 + KCl$), forming *phosphorus oxychloride*, $POCl_3$ (Brodie). This compound is also formed by the first action of water on phosphoric chloride; for example, if two vessels, one containing phosphoric chloride and the other water, are placed under a bell jar, after a certain time the crystals of the chloride disappear and hydrochloric acid passes into the water. The aqueous vapour acts on the pentachloride, and the following reaction occurs: $PCl_5 + H_2O =$

p. 310), sulphuric acid, &c. The products of disruption must here be phosphorous chloride, PCl_3, and chlorine, Cl_2, bodies which easily re-form phosphoric chloride, PCl_5, at a lower temperature, because the latter may be distilled. This decomposition of phosphoric chloride in its conversion into vapour is confirmed by the fact that the vapour of this almost colourless substance shows the greenish yellow colour proper to chlorine. This dissociation of phosphoric chloride has been considered by some chemists as a sign that phosphorus, like nitrogen, does not give volatile compounds of the type PX_5, and that such substances are only obtained as unstable molecular compounds which break up when distilled; for example, PH_3,HI; PCl_3,Cl_2, NH_3,HCl, &c. However this may be, there are perfectly definite, although perhaps unstable, compounds belonging to the type PX_5. Furthermore, Würtz in 1870 observed that when mixed with the vapour of phosphorous chloride, the vapour of phosphoric chloride distils (from 160° to 190°) over perfectly colourless, and has a density which is really near to the formula—namely, to 104—and the same density was determined for the pentachloride in an atmosphere of chlorine. Hence at low temperatures and in admixture with one of the products of dissociation, there is no longer that decomposition which occurs at higher temperatures—that is, we here have a case of dissociation proceeding at moderate temperatures.

An important proof in favour of the type PX_5 is exhibited by phosphorus pentafluoride PF_5, obtained by Thorpe as a colourless gas which only corrodes glass after the lapse of time; it may be kept under mercury, and has a normal density. It is formed when liquid arsenic trifluoride, AsF_3, is added to phosphoric chloride surrounded by a freezing mixture: $3PCl_5 + 5AsF_3 = 3PF_5 + 5AsCl_3$.

$POCl_3 + 2HCl$, the result being that liquid phosphorus oxychloride is found in one vessel, and a solution of hydrochloric acid in the other. However, an excess of water directly transforms phosphoric chloride into orthophosphoric acid, $PCl_5 + 4H_2O = PH_3O_4 + 5HCl$.[26]

The above chlorine compounds serve not only as a type of the chloranhydrides, but also as a means for the preparation of other *acid chloranhydrides*. Thus the conversion of acids RHO into chloranhydrides, RCl, is generally accomplished by means of *phosphorus pentachloride*. This fact was discovered by Chancel, and adopted by Gerhardt as an important means for studying organic acids. By this means organic acids, containing, as we know, RCOOH (where R is a hydrocarbon group, and where carboxyl may repeat itself several times by replacing the hydrogen of hydrocarbon compounds), are converted into their chloranhydrides, RCOCl. With water they again form the acid, and resemble the chloranhydrides of mineral acids in their general properties.

As carbonic acid, $CO(OH)_2$, contains two hydroxyl groups, therefore its perfect chloranhydride, $COCl_2$, *carbonic oxychloride*, *carbonyl chloride*, or *phosgene gas*, contains two atoms of chlorine, and differs from the chloranhydrides of organic acids in that in them one atom of chlorine is replaced by the hydrocarbon radicle RCOCl, if R is a monatomic radicle giving a hydrocarbon RH. It is evident, on the one hand, that in RCOCl the hydrogen is replaced by the radicle COCl, which is also able to replace several atoms of hydrogen (for example, $C_2H_4(COCl)_2$ corresponds with the bibasic succinic acid); and, on the other hand, that the reactions of the chloranhydrides of organic acids will answer to the reactions of carbonyl chloride, as the reactions of the acids themselves answer to carbonic acid. Carbonyl

[26] Phosphorus oxychloride is obtained by the action of phosphoric chloride on hydrates of acids (because alkalis decompose phosphorus oxychloride), according to the equation $PCl_5 + RHO = POCl_3 + RCl + HCl$, where RHO is an acid. The reaction only proceeds according to this equation with monobasic acids, but then RCl is volatile, and therefore a mixture is obtained of two volatile substances, the acid chloride and phosphorus oxychloride, which are sometimes difficult to separate; whilst if the hydrate be polybasic the reaction frequently proceeds so that an anhydride is formed: $RH_2O_2 + PCl_5 = RO + POCl_3 + 2HCl$. If the anhydride is non-volatile (like boric), or easily decomposed (like oxalic), then it is easy to obtain pure oxychloride. Thus phosphorus oxychloride is often prepared by acting on boric or oxalic acid with phosphoric chloride. It is also formed when the vapour of phosphoric chloride is passed over phosphoric anhydride, $P_2O_5 + 3PCl_5 = 5POCl_3$. This forms an excellent example in proof of the fact that the formation of one substance from two does not necessarily show that the resultant compound contains the molecules of these substances in its molecule. But other oxychlorides of phosphorus are also formed by the interaction of phosphoric anhydride and chloride; thus at 200° the chloranhydride, PO_2Cl, or chloranhydride of metaphosphoric acid, is formed.

chloride is obtained directly from dry carbon monoxide and chlorine[27] exposed to the action of light, and forms a colourless gas, which easily condenses into a liquid, boiling at +8°, sp. gr. 1·43, and having the suffocating odour proper to all chloranhydrides. Like all chloranhydrides, it is immediately decomposed by water, forming carbonic anhydride, according to the equation $COCl_2 + H_2O = CO_2 + 2HCl$, and thus expresses the type proper to all chloranhydrides of both mineral and organic acids.[28]

In order to show the general method for the preparation of acid chloranhydrides, we will take that of acetic acid, $CH_3 \cdot COOH$, as an example. Phosphorus pentachloride is placed in a glass retort, and acetic acid poured over it; hydrochloric acid is then evolved, and the substance distilling over directly after is a very volatile liquid, boiling at 50°, and having all the properties of the chloranhydrides. With water it forms hydrochloric and acetic acids. The reaction here taking place may be explained thus: the substitution of the oxygen taken from the

[27] The direct action of the sun's rays, or of magnesium light, is necessary to start the reaction between carbonic oxide and chlorine, but when once started it will proceed rapidly in diffused light. An excess of chlorine (which gives its coloration to the colourless phosgene) aids the completion of the reaction, and may afterwards be removed by metallic antimony. Porous substances, like charcoal, aid the reaction. Phosgene may be prepared by passing a mixture of carbonic anhydride and chlorine over incandescent charcoal. Lead or silver chloride, when heated in a current of carbonic oxide, also partially form phosgene gas. Carbon tetrachloride, CCl_4, also forms it when heated with carbonic anhydride (at 400°), with phosphoric anhydride (200°), and most easily of all with sulphuric anhydride ($2SO_3 + CCl_4 = COCl_2 + S_2O_5Cl_2$, this is pyrosulphuryl chloride). Chloroform, $CHCl_3$, is converted into carbonyl chloride when heated with $SO_2(OH)Cl$ (the first chloranhydride of sulphuric acid); $CHCl_3 + SO_3HCl = COCl_2 + SO_2 + 2HCl$ (Dewar), and when oxidised by chromic acid.

Among the reactions of phosgene we may mention the formation of urea (Vol. I. p. 397) with ammonia, and of carbonic oxide when heated with metals.

[28] Among the chloranhydrides of the inorganic acids we shall describe some which correspond with sulphuric acid in the following chapter; and here we will mention that when hydrochloric acts on nitric acid (aqua regia, Vol. I. p. 461) there is formed, besides chlorine, the oxychlorides NOCl and NO_2Cl, which may be regarded as chloranhydrides of nitric and nitrous acids (nitrogen chloride, Vol. I. p. 470). The former boils at −5°, the latter at +5°, the specific gravity of the first at −12° = 1·416, and at −18° = 1·433 (Geuther), and of the second = 1·3; the first is obtained from nitric oxide and chlorine, the second from nitric peroxide and chlorine, and also by the action of phosphoric chloride on nitric acid. If the gases evolved by aqua regia be passed into cold and strong sulphuric acid, they form crystals of the composition $NHSO_5$ (like chamber crystals), which melt at 86°, and with sodium chloride form acid sodium sulphate and the oxychloride NOCl. This chloranhydride of nitric acid is termed *nitrosyl chloride*.

Cyanogen chloride, CNCl, is the gaseous chloranhydride of cyanic acid; it is formed by the action of chlorine on aqueous mercury cyanide, $Hg(CN)_2 + 2Cl_2 = HgCl_2 + 2CNCl$. When chlorine acts on cyanic acid, it forms not only this cyanogen chloride, but also polymerides of it—a liquid one, boiling at 18°, and a solid one, boiling at 190°. The latter corresponds with cyanuric acid, and consequently contains $C_3N_3Cl_3$. Details concerning these substances must be looked for in works on organic chemistry.

acetic acid (from its carboxyl) by two atoms of chlorine from the PCl_5 should be as follows: $CH_3{\cdot}COOH + PCl_5 = CH_3{\cdot}COHCl_2 + POCl_3$. But the compound $CH_3{\cdot}COHCl_2$ does not exist in a free state (because it would indicate the possibility of the formation of compounds of the type CX_6, and carbon only gives those of the type CX_4); it therefore splits up into HCl and the chloranhydride $CH_3{\cdot}COCl$. The general scheme for the reaction of phosphorus pentachloride with hydrates ROH is exactly the same as with water; namely, ROH with PCl_5 gives $POCl_3 + HCl + RCl$—that is a chloranhydride.[28b]

Containing, as they do, chlorine, which easily reacts with hydrogen, phosphorus pentachloride, trichloride, and oxychloride enter into

[28b] The same phenomenon takes place in the reaction of phosphorus pentachloride with water, H_2O, and other hydrates, RHO: $R(OH) + PCl_5 = RCl + HCl + POCl_3$. This reaction indeed proceeds very easily and cleanly with a number of hydroxides, if they do not react on hydrochloric acid and phosphorus oxychloride, which is the case when they have alkaline properties. When the hydroxide is taken in excess, it not unfrequently happens that the elements of water are taken up: $R(OH)_2 + PCl_5 = RO + 2HCl + POCl_3$. The phosphorus pentachloride and the anhydride RO may then be converted into chloranhydride, $RO + PCl_5 = RCl_2 + POCl_3$—that is, it aids the substitution of O by Cl_2. Thus carbonyl chloride, $COCl_2$, boron chloride, $2BCl_3$, and succinic chloride, $C_4H_4O_2Cl_2$, &c., are respectively obtained by the action of phosphoric chloride on carbonic, boric, and succinic anhydrides. Phosphorus pentachloride reacts in a similar manner on the aldehydes, RCHO, forming $RCHCl_2$, and on the chloranhydrides themselves—for example, with acetic chloride, $CH_3{\cdot}COCl$ (when heated in a closed tube), it forms a substance having the composition $CH_3{\cdot}CCl_3$. Similar chlorine products are formed together with phosphorus oxychloride, but they are often easily separated from it.

Phosphorus trichloride and oxychloride act in a similar manner to phosphoric chloride. When phosphorus trichloride acts on an acid, then $3RHO + PCl_3 = 3RCl + P(HO)_3$. If a salt is taken, then by the action of phosphorus oxychloride, a corresponding chloranhydride and salt of orthophosphoric acid are easily formed: $3R(KO) + POCl_3 = 3RCl + PO(KO)_3$. The chloranhydride RCl is always more volatile than its corresponding acid, and distils over before the hydrate RHO. Thus acetic acid boils at 117°, and its chloranhydride at 50°. Phosphoric and phosphorous acids are very slightly volatile, whilst their chloranhydrides are comparatively easily converted into vapour. The faculty of the chloranhydrides to react at the expense of their own chlorine determines their great importance in chemistry. For instance, suppose we require to know the molecular formula of some hydrate which does not pass into a state of vapour and does not give a chloranhydride with hydrochloric acid—that is, which has not any basic or alkaline properties; we must then endeavour to obtain this chloranhydride by means of phosphoric chloride, and it frequently happens that the corresponding chloranhydride is volatile. The resultant chloranhydride is then converted into vapour, and its composition is determined; and if we know its composition we are able to judge that of its corresponding hydrate. So, for example, from the formula of silicon chloride, $SiCl_4$, or of boron chloride, BCl_3, we can judge the composition of their corresponding hydrates, $Si(HO)_4$, $B(HO)_3$. Having obtained the chloranhydride RCl or RCl_n, it is possible by its means to obtain many other compounds of the same radicle R according to the equation $MX + RCl = MCl + RX$. M may be = H, K, Ag, or other metals. The reaction proceeds thus if M forms a stable compound with chlorine—for example, silver chloride, hydrochloric acid, and R, an unstable substance. Therefore, a chloranhydride is frequently employed for the formation of other compounds of a given radicle; for instance, with ammonia they form amides RNH_2, and with salts ROK anhydrides R_2O, &c.

reaction with ammonia, and give a series of amide and nitrile compounds of phosphorus. Thus, for example, when ammonia acts on the oxychloride we obtain sal-ammoniac (which is afterwards removed by water) and an orthophosphoric triamide, $PO(NH_2)_3$, as a white insoluble powder on which dilute acids and alkalis do not act, but which, when fused with potassium hydroxide, gives potassium phosphate and ammonia like other amides. When ignited, the triamide disengages ammonia and forms the nitrile PON, just as urea, $CO(NH_2)_2$, disengages ammonia and forms the nitrile CONH. This nitrile, called *monophosphamide*, PON, naturally corresponds with metaphosphoric acid, namely, with its ammonium salt. $NH_4PO_3 - H_2O = PO_2 \cdot NH_2$, an as yet unknown amide, and $PO_2 \cdot NH_2 - H_2O$ gives the nitrile PON. This relation is confirmed by the fact that PON, moistened with water, gives metaphosphoric acid when ignited. It is the analogue of nitrous oxide, NON. It is a very stable compound, more so than the preceding.[29]

[29] The reaction of ammonia on phosphorus pentachloride is more complex than the preceding. This is readily understood: to the oxychloride, $POCl_3$, there corresponds a hydrate $PO(OH)_3$, and a salt $PO(NH_4O)_3$, and consequently also an amide $PO(NH_2)_3$, whilst the pentachloride, PCl_5, has no corresponding hydrate $P(OH)_5$, and therefore there is no amide $P(NH_2)_5$. The reaction with ammonia will be of two kinds: either instead of 5 mol. NH_3, only 3 mol. NH_3 or still less acts; *i.e.*, $PCl_2(NH_2)_3$, $PCl_3(NH_2)_2$, &c., are formed, or else the pentachloride acts like a mixture of chlorine with the trichloride, and then as the result there are obtained the products of the action of chlorine on those amides which are formed from phosphorus trichloride and ammonia. It would appear that both kinds of reaction proceed simultaneously, but both kinds of products are unstable, at all events complex, and in the result there is obtained a mixture containing sal-ammoniac, &c. The products of the first kind should react with water, and we shall obtain, for example, $PCl_3(NH_2)_2 + 2H_2O = 3HCl$ and $PO(HO)(NH_2)_2$. This substance has not actually been obtained, but the compound $PONH(NH_2)$ derived from it by elimination of the elements of water is known, and is termed *diphosphamide*; it is, however, more probable that it is a nitrile than an amide, because amides only contain the group NH_2. It is a colourless, stable, insoluble powder, which possibly corresponds with pyrophosphoric acid, more especially as when heated it evolves ammonia and gives and leaves phosphoryl nitride, PON—that is, the nitrile of metaphosphoric acid. The amide corresponding with the pyrophosphate $P_2O_5(NH_4O)_4$ should be $P_2O_5(NH_2)_4$, and the nitriles corresponding to the latter would be $P_2O_2N(NH_2)_3$, $P_2ON_2(NH_2)_2$, and $P_2N_3(NH_2)$. The composition of the first is the same as that of the above diphosphamide. The third pyrophosphoric nitrile has a formula $P_2N_4H_2$, and this is the composition of the body known as *phospham*, PHN_2. Indeed, phospham has been obtained by heating the products of the action of ammonia on phosphoric chloride, as an insoluble and alkaline powder, which gives ammonia and phosphoric acid when subjected to the action of water. The same substance is obtained by the action of ammonium chloride on phosphoric chloride ($PNCl_2$ is first formed, and reacts further with ammonia, forming phospham), and by igniting the mass which proceeds from the action of ammonia on phosphorus trichloride. Formerly the composition of phospham was supposed to be PHN_2, now there is reason to think that its molecular weight is $P_3H_3N_6$ (see later).

The above compounds correspond with normal salts, but nitriles and amides corresponding to acid salts are also possible, and they will be acids. For example, the amide

The most important analogue of phosphorus is *arsenic*, the metallic aspect of which and the general character of its compounds at once recalls the metals. The hydrate of its highest oxide, arsenic acid (ortho-arsenic acid), H_3AsO_4, is an oxidising agent, and gives up a portion of its oxygen to many other substances; but, nevertheless, it is very like phosphoric acid. Mitscherlich established the conception of isomorphism by comparing the salts of these acids together.[30]

$PO(HO)_2(NH_2)$, and its nitrile, which will be either $PN(HO)_2$ or $PO(HO)(NH)$, but at all events of the composition PNH_2O_2, and having acid properties. The ammonium salt of this *phosphonitrilic acid* (it is called phosphamic acid), $PNH(NH_4)O_2$, is obtained by the action of ammonia on phosphoric anhydride, $P_2O_5+4NH_3=H_2O+2PNH(NH_4)O_2$. A non-crystalline soluble mass is thus formed, which is dissolved in a dilute solution of ammonia and precipitated with barium chloride, and the resultant barium salt is then decomposed with sulphuric acid, and thus a solution of the acid of the above composition is obtained.

It is evident from the theory of the formation of amides and nitriles (Chapter IX.) that very many compounds of this kind can correspond with the acids of phosphorus; but as yet only a few are known. The easy transitions of the ortho-, meta-, and pyro-phosphoric acids, by means of the hydrogen of ammonia, into the lower acids, and conversely, tend to complicate the study of this vast class of compounds, and it is rarely that the nature of a product thus obtained can be judged from its composition; and this all the more that instances of isomerism and polymerism, of mixture between water of crystallisation and of constitution, &c., are here possible. Many data are yet wanting in order to be able to form a true judgment as to the composition and structure of such compounds. As the best proof of this we will describe the very interesting and most fully investigated compound of this class, $PNCl_2$, called *chlorophosphamide*, or nitrogen chlorophosphorite. It is formed in small quantities when the vapour of phosphoric chloride is passed over ignited sal-ammoniac. It is clear that phosphorous chloride, ammonia, chlorine, and hydrochloric acid are all acting in this case. It might be thought that the formation of $PNCl_2$ corresponds with the simple reaction $PCl_5+NH_3=3HCl+PNCl_2$, but in reality the reaction is more complex, as is seen by the properties of the product. The chlorine in it is very stable—quite different from that in phosphoric chloride. Indeed, the resultant substance is not only insoluble in water (but soluble in alcohol and ether), but it is not moistened by it, and distils over, together with steam, without being decomposed. In a free state it easily crystallises in colourless prisms, fuses at 114°, boils at 250° (Gladstone, Wichelhaus), and when fused with potash gives potassium chloride and the amidonitryl of phosphoric acid. Judging from its formula and the simplicity of composition and reactions, it might be thought that the molecular weight of this substance would be expressed by the formula PCl_2N, that it corresponds with PON and with PCl_5 (like $POCl_3$), with the substitution of Cl_3 by N, just as in $POCl_3$ two of chlorine are replaced by oxygen; but all these approximations are incorrect, because its vapour density (referred to hydrogen—Gladstone, Wichelhaus) =182—that is, the molecular formula must be three times greater, $P_3N_3Cl_6$. The polymerisation (tripling) is here of exactly the same kind as with the nitriles.

[30] It is necessary to remark that although arsenic is so closely analogous to phosphorus (especially in the higher forms of combination, RX_3 and RX_5), at the same time it exhibits a certain resemblance and even isomorphism with the corresponding compounds of sulphur (especially the metallic compounds of the type MAs, corresponding with MS). Thus compounds containing metals, arsenic, and sulphur are very frequently met with in nature. Sometimes the relative amounts of arsenic and sulphur varies, so that an isomorphous substitution between the arsenides and sulphides must be recognised. Besides ordinary pyrites, FeS_2, iron forms an arsenide, $FeAs_2$, and an arsenical

Arsenic occurs *in nature*, not only combined with metals, but also, although rarely, native and also in combination with sulphur in two minerals—one red, *realgar*, As_2S_2, and the other yellow, *orpiment*, As_2S_3. Arsenic occurs, but more rarely, in the form of salts of arsenic acid—for instance, the so-called cobalt and nickel blooms, two minerals which are found together with other cobalt ores, are the arsenates of these metals. Arsenic is also found in certain clays (ochres), and has been discovered in small quantities in some mineral springs, but it is in general of rarer occurrence in nature than phosphorus. Arsenic is most frequently extracted from arsenical pyrites, FeSAs, which, when roasted without access of air, evolves the vapour of arsenic, ferrous sulphide being left behind. It is also obtained by heating arsenious anhydride with charcoal, in which case carbonic oxide is evolved. In general, the oxides and other compounds are very easily reduced to metals. Solid *arsenic* is a steel-grey, brittle *metal*, having a bright lustre and scaly structure. Its sp. gr. is 5·7. It is opaque and infusible, but volatilises as a yellow vapour, which on cooling deposits rhombohedral crystals. The vapour density of arsenic is 150 times greater than that of hydrogen—that is, its molecule, like that of phosphorus, contains 4 atoms, As_4. When heated in the air, arsenic easily oxidises into white arsenious anhydride, As_2O_3, but even at the ordinary temperature it loses its lustre (becomes dull), owing to the formation of a coating of a lower oxide. The latter appears to be as volatile as arsenious anhydride, and it is probable that it is owing to the presence of this compound that the vapours of arsenious compounds, when heated with charcoal (for example, in the reducing flame of a blow-pipe), have the characteristic smell of garlic, because the vapour of arsenic itself has not this odour.

Arsenic easily combines with bromine and chlorine ;[31] nitric acid

pyrites containing both sulphur and arsenic, which from its composition, FeAsS or FeS_2FeAs_2, resembles the two preceding.

[31] Hydrochloric acid dissolves arsenious anhydride in considerable quantities, and this is probably owing to the formation of unstable compounds in which the arsenious anhydride plays the part of a base. A compound called *arsenious oxychloride*, having the composition AsOCl, is even known. It is formed when arsenious anhydride is added little by little to boiling arsenic trichloride, $As_2O_3 + AsCl_3 = 3AsOCl$. It is a transparent substance, which fumes in air, and combines with water to form a crystalline mass having the composition $As_2(OH)_4Cl_2$. When heated it decomposes into arsenious chloride and a fresh oxychloride of a more complex composition, $As_6O_8Cl_2$. Arsenic trichloride, when treated with a small quantity of water, forms the crystalline compound, $As_2(HO)_4Cl_2$, mentioned above. These compounds resemble the basic salts of bismuth and aluminium. The existence of these compounds shows that arsenic is of a more metallic or basic character than phosphorus, because phosphorus trichloride does not form such oxychlorides. Nevertheless *arsenic trichloride*, $AsCl_3$, resembles phosphorus trichloride in many respects. It is obtained by the direct action of chlorine on arsenic, or by

and aqua regia also oxidise it into the higher oxide, or rather its hydrate, arsenic acid.[32] As far as is known, it does not decompose steam, and

distilling a mixture of common salt, sulphuric acid, and arsenious anhydride. The latter mode of preparation already indicates the basic properties of the oxide. Arsenious chloride is a colourless oily liquid, boiling at 130°, and having a sp. gr. of 2·20. It fumes in air like other chloranhydrides, but is much more slowly and feebly decomposed by water than phosphorus trichloride. A considerable quantity of water is required for its perfect decomposition into hydrochloric acid and arsenious anhydride. It forms an excellent example of the transition from true metallic chlorides to true chloranhydrides of the acids. It does not combine with chlorine, so that it does not form a pentachloride, $AsCl_5$, like phosphorus. *Arsenic tribromide*, $AsBr_3$, is formed as a crystalline substance, fusing at 20° and boiling at 220°, by the direct action of metallic arsenic on a solution of bromine in carbon bisulphide, the latter being then evaporated. The specific gravity of arsenic tribromide is 3·36. Crystalline arsenic tri-iodide, AsI_3, having a sp. gr. 4·39, may be obtained in a like manner; it may be dissolved in water, and on evaporation separates out from the solution in an anhydrous state—that is, it is not decomposed—and consequently behaves like metallic salts. *Arsenic trifluoride*, AsF_3, is obtained by heating fluor spar and arsenious anhydride with sulphuric acid. It is a fuming, colourless, and very poisonous liquid, which boils at 63° and has a sp. gr. of 2·73. It is decomposed by water, but the products of decomposition have not yet been investigated. It is very remarkable that fluorine forms a pentafluoride of arsenic also, although this compound has not yet been obtained in a separate state, but only in combination with potassium fluoride. This compound, K_3AsF_8, is formed as prismatic crystals when potassium arsenate, K_3AsO_4, is dissolved in hydrofluoric acid.

[32] *Arsenic acid*, H_3AsO_4, corresponding with orthophosphoric acid, is formed by oxidising arsenious anhydride with nitric acid, and evaporating the resultant solution until it attains a sp. gr. of 2·2; on cooling it separates in crystals having the above composition. This hydrate corresponds with the normal salts of arsenic acid; but on dissolving in water (without heating) and cooling a strong solution, crystals containing a greater amount of water, namely, $(AsH_3O_4)_2H_2O$, separate. This water, like water of crystallisation, is very easily expelled at 100°. At 120° crystals having a composition identical with that of pyrophosphoric acid, $As_2H_4O_7$, separate, but water, on dissolving this hydrate with the development of heat, forms a solution in no way differing from a solution of ordinary arsenic acid, so that it is not an independent pyroarsenic acid that is formed. Neither is there any true analogue of metaphosphoric acid, although the compound $AsHO_3$ is formed at 200°, and on solidifying forms a mass having a pearly lustre and sparingly soluble in cold water; but on coming into contact with warm water it becomes very hot, and gives ordinary ortharsenic acid in solution. Arsenic acid forms three series of salts, which are perfectly analogous to the three series of orthophosphates. Thus the normal salt, K_3AsO_4, is formed by fusing the other potassium arsenates with potassium carbonate; it is soluble in water, and crystallises in needles, which do not contain water. Di-potassium arsenate, K_2HAsO_4, is formed in solution by mixing potassium carbonate and arsenic acid until carbonic anhydride ceases to be evolved; it does not crystallise, and has an alkaline reaction; hence it corresponds perfectly with the sodium phosphate. As was mentioned above, arsenic acid itself acts as an oxidising agent; for example, it is used in the manufacture of aniline dyes, for oxidising the aniline, and it is prepared in large quantities for this purpose. When sulphuretted hydrogen is passed through its solution, sulphuric acid and arsenious anhydride are obtained in solution. Arsenic acid is very easily soluble in water, and its solution has an exceedingly acid reaction, and when boiled with hydrochloric acid evolves chlorine, like selenic, chromic, manganic, and certain other higher metallic acids.

Arsenic anhydride, As_2O_5, is produced when arsenic acid is heated to redness. It must be carefully heated, as at a bright red heat it decomposes into oxygen and arsenious anhydride. Arsenic anhydride is an amorphous substance almost entirely insoluble in

it acts exceedingly slowly on those acids, like hydrochloric, which are not capable of oxidising.

Arseniuretted hydrogen, arsine, AsH_3, resembles phosphuretted hydrogen in many respects. This colourless gas, which liquefies into a mobile liquid at $-40°$, has a disagreeable garlic-like odour, is only slightly soluble in water, and is exceedingly poisonous. Even in a small quantity it causes great suffering, and if present to any considerable amount in air it even causes death. The other compounds of arsenic are also equally poisonous, with the exception of the insoluble sulphur compound and arsenic acid. Arseniuretted hydrogen, AsH_3, is obtained by the action of water on the alloy of arsenic and sodium, sodium hydroxide and arseniuretted hydrogen being formed. It is also formed by the action of sulphuric acid on the alloy of arsenic and zinc: $Zn_3As_2 + 3H_2SO_4 = 2AsH_3 + 3ZnSO_4$.[33] The oxygen compounds of arsenic are very easily reduced by the action of hydrogen at the moment of its evolution from acids, and the reduced arsenic then combines with the hydrogen; therefore, if a certain amount of an oxygen compound of arsenic be put into an apparatus containing zinc and sulphuric acid (and thus serving for the evolution of hydrogen) then the hydrogen evolved will contain arseniuretted hydrogen. In this case it is diluted with a considerable amount of hydrogen. But its presence in the most minute quantities may be easily recognised from the fact that it is *easily decomposed* by heat into metallic arsenic and hydrogen, and therefore if such impure hydrogen be passed through a moderately-heated tube metallic arsenic will be deposited as a bright layer on the part of the tube which was heated. This reaction is so sensitive that it enables the most minute traces of arsenic to be discovered; hence it is employed in medical jurisprudence, as a test in poisoning cases. It is easy to discover the presence of arsenic in common zinc, copper, sulphuric and hydrochloric acids, &c., by this method. It is evident that in testing for poison by Marsh's apparatus it is necessary to take zinc and sulphuric acid quite free from arsenic. The arsenic deposited in the tube may be driven from one place to another in the current of hydrogen evolved, owing to its volatility. This forms a distinctive feature between arseniuretted and antimoniuretted hydrogen, which is decomposed by heat in just the same way as arseniuretted hydrogen.

water, but it attracts moisture from the air, deliquesces, and passes into the acid. Hot water produces this transformation with great ease.

[33] The formation of arseniuretted hydrogen is accompanied by the absorption of 37000 heat units, while phosphine evolves 18000 (Ogier), and ammonia 27000. Sodium (0·6 p.c.) amalgam, with a strong solution of As_2O_3, gives a gas containing 86 vols. of arsenic and 14 vols. of hydrogen (Cavazzi).

If hydrogen contains arseniuretted hydrogen it also gives metallic arsenic when it burns, because in the reducing flame of hydrogen the oxygen attracted combines entirely with the hydrogen and not with the arsenic, so that if a cold object, such as a piece of china, be held in

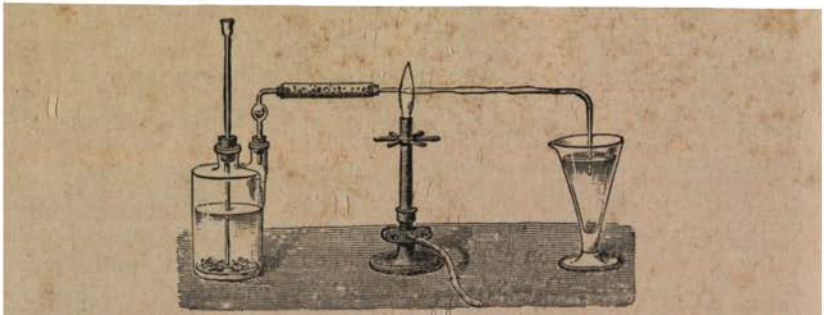

FIG. 84.—Formation and decomposition of arseniuretted hydrogen. Hydrogen is evolved in the Woulfe's bottle, and when the gas comes off, a solution containing arsenic is poured through the funnel. The presence of AsH_3 is recognised from the deposition of a mirror of arsenic when the gas-conducting tube is heated. If the escaping hydrogen be lighted, and a porcelain dish be held in the flame, then a patch of arsenic is deposited on it. The gas is dried by passing through the tube containing calcium chloride. This apparatus is used for the detection of arsenic by Marsh's test.

the hydrogen flame the arsenic will be deposited upon it as a metallic spot.[34]

The most common compound of arsenic is the solid and volatile *arsenious anhydride*, As_2O_3, which corresponds with phosphorous and nitrous anhydrides. This very poisonous, colourless, and sweet-tasting

[34] This spot, or the metallic ring which is deposited on the heated tube, may easily be tested as to whether it is really due to arsenic or proceeds from some other substance reduced in the hydrogen flame—for instance, carbon or antimony. The necessity for distinguishing arsenic from antimony is all the more frequently encountered in medical jurisprudence, from the fact that preparations of antimony are very frequently used as medicine, and antimony behaves in the hydrogen apparatus just like arsenic, and therefore in making an investigation for poisoning by arsenic it is easy to mistake it for antimony. The best method to distinguish between the metallic spots of arsenic and antimony is to test them with a solution of sodium hypochlorite, free from chlorine, because this will dissolve arsenic and not antimony. Such a solution is easily obtained by the double decomposition of solutions of sodium carbonate and bleaching powder. A solution of potassium chlorate acts in the same manner, only more slowly. Further particulars must be looked for in analytical works.

Arseniuretted hydrogen, like phosphuretted hydrogen, is only slightly soluble in water, and has no alkaline properties—that is, it does not combine with acids, and acts as a reducing agent. When passed into a solution of silver nitrate it gives a blackish brown precipitate of metallic silver, the arsenic being oxidised. In acting on copper sulphate and similar salts, arseniuretted hydrogen sometimes forms arsenides—*i.e.*, it reduces the metallic salt with its hydrogen, and is itself reduced to arsenic. Sulphuric, and even hydrochloric, acid reduces arseniuretted hydrogen to arsenic, and it is still more easily decomposed by arsenious chloride, and with phosphorous chloride it gives the compound PAs. Arseniuretted hydrogen gives metallic arsenic with an acid solution of arsenious anhydride.

substance is generally known under the name of arsenic, or *white arsenic*. The corresponding hydrate is as yet unknown, although the anhydride is soluble in water; but its solutions, when heated, yield crystals of arsenious anhydride. It is mainly prepared for the dyer, and as a means for poisoning vermin, sometimes in medicine, and also as a means for the preparation of all other compounds of arsenic. It is obtained as a bye product in roasting cobalt and other ores containing arsenic. Arsenical pyrites are sometimes purposely roasted for the extraction of arsenious anhydride. When arsenical ores are burnt in the air the sulphur and arsenic are converted into the oxides As_2O_3 and SO_2. The former is a solid at the ordinary temperature, and the latter gaseous, and therefore the arsenious anhydride is deposited as a sublimate in the cooler portion of the flues through which the vapours escape from the furnace. It collects in condensing chambers especially constructed in the flues. The deposit is collected, and after being distilled gives arsenious anhydride in the form of a vitreous non-crystalline mass. This is one of the varieties of arsenious anhydride, which is also known in two crystalline forms. When sublimed—*i.e.*, when it rapidly passes from the state of vapour to the solid state—it appears in the regular system in the form of octahedra.[35] It is obtained in the same form when it is crystallised from acid solutions. The sp. gr. of the crystals is 3·7. The other crystalline form (in prisms) belongs to the rhombohedral system, and is also formed by sublimation, when the crystals are deposited on a heated surface, or when it is crystallised from alkaline solutions.[36]

[35] According to Mitscherlich's determination, the vapour density of arsenious anhydride is 199(H=1)—that is, it answers to the molecular formula As_4O_6. Probably this is connected with the fact that the molecule of free arsenic contains As_4. Meyer and Biltz, however, showed (1889) that at a temperature of about 1700° the vapour density of arsenic corresponds with the molecule As_2, and not As_4, as at lower temperatures.

[36] Arsenious anhydride is obtained in an amorphous form after prolonged heating at a temperature near to that at which it volatilises, or, still better, by heating it in a closed vessel. It then fuses to a colourless liquid, which on cooling forms a transparent vitreous mass, whose specific gravity is almost the same as that of the crystalline anhydride (slightly less). On cooling, this vitreous mass undergoes an internal variation, in which it crystallises and becomes opaque, and acquires the appearance of porcelain. The following difference between the vitreous and opaque varieties is very remarkable: when the vitreous variety is dissolved in strong and hot hydrochloric acid it gives crystals of the anhydride on cooling, and this *is accompanied by the emission of light* (which is visible in the dark), and the entire liquid glows as the crystals begin to separate. The opaque variety does not emit light when the crystals separate from its hydrochloric acid solution. It is also remarkable that the vitreous variety passes into the opaque form when it is pounded—that is, under the action of a series of blows. Thus, several varieties of arsenious anhydride are known, but as yet they are not characterised by any special chemical distinctions, and even differ but little in their specific gravities, and therefore it cannot be said that the above differences are due to any isomeric transformations—that

Solutions of arsenious anhydride have a sweet metallic taste, and give *a feeble acid reaction.* Its solubility increases with the admixture of acids and alkalis. This shows the property of arsenious anhydride of forming salts with acids and alkalis. And, in fact, compounds of it with hydrochloric acid and with the alkali oxides are known.[37] If silver nitrate be added to a solution of arsenious anhydride, it does not give any precipitate unless a certain amount of the arsenious anhydride is saturated with an alkali—for instance, ammonia. It then gives a precipitate of silver arsenite, Ag_3AsO_3. This is yellow, soluble in an excess of ammonia, and anhydrous; it distinctly shows that arsenious acid is tribasic, and that it differs in this respect from phosphorous acid, in which only two atoms of hydrogen can be replaced by metals.[38] The feeble acid character of arsenious anhydride is

is, to a replacement of the atoms in the molecule—but probably only depend on a difference in the distribution of the molecules, or, in other terms, are physical and not chemical variations. One part of the vitreous anhydride requires twelve parts of boiling water for its solution, or twenty-five parts at the ordinary temperature. The opaque variety is less soluble, and at the ordinary temperature requires about seventy parts of water for its solution.

[37] Arsenious anhydride does not oxidise in air, either in a dry state or in solution, but in the presence of alkalis it absorbs oxygen from the air, and acts as an excellent reducing agent. This probably is connected with the fact that arsenic acid is much more energetic than arsenious acid, and that it is arsenic acid which is formed by the oxidation of the latter in the presence of alkalis. Arsenious anhydride is easily reduced to arsenic by many metals, even by copper.

[38] The feeble acid properties of arsenious anhydride are seen from the fact that if it be dissolved in ammonia water, and then a still stronger solution of ammonia be added, prismatic crystals separate, having the composition of ammonium metarsenite, NH_4AsO_3. This ammonium salt deliquesces in air, and loses all its ammonia. The magnesium salt is tri-metallic, $Mg_3(AsO_3)_2$; it is insoluble in water, and is formed by mixing an ammoniacal solution of arsenious anhydride with an ammonical solution of a magnesium salt. It is insoluble even in ammonia, although it dissolves in an excess of acids. Magnesium hydroxide gives the same salt with arsenious solutions, and hence magnesia is one of the best antidotes against arsenic poisoning. *The arsenites of copper* are much used in the manufacture of dyes, and more especially of pigments. They are distinguished by their insolubility in water and by their remarkably vivid green colour, but at the same time by their poisonous character. Not only do such pigments applied to wall papers or materials easily dust off from them, but they give exhalations containing arsenic. The cupric salts, CuX_2, when mixed with an alkaline solution of arsenious acid, give a green precipitate of a copper salt called *Scheele's green.* Its composition is probably $CuHAsO_3$. Ammonia dissolves it, and gives a colourless solution, containing cuprous arsenate—that is, the cupric compound is reduced and the arsenic subjected to a further oxidisation. The so-called *Schweinfurt green* was still more used, especially in former times; it is also an insoluble green cupric salt, which resembles the preceding in many respects, but has a different tint. It is prepared by mixing boiling solutions of arsenious acid and cupric acetate. Arsenious acid forms an insoluble compound with ferric hydroxide, resembling the phosphate; and this is the reason why freshly-precipitated oxide of iron is employed as an *antidote for arsenic.* The freshly-precipitated oxide of iron, taken immediately after poisoning by arsenic, converts the arsenious acid into an insoluble state, and forms a compound on which the acids of the stomach have no action, and therefore the poisoning cannot proceed. It must be further observed that *arsenic is poisonous*

confirmed by the formation of saline compounds with acids. In this respect the most remarkable example is the anhydrous compound with sulphuric acid, and having the composition As_2O_3,SO_3. It is formed in the roasting of arsenical pyrites in those spaces where the arsenious anhydride condenses, and this is the more remarkable as sulphurous anhydride is converted into sulphuric anhydride, SO_3, at the expense of the oxygen of the air in the process, which would seem to be a consequence of the character of arsenious anhydride. The compound in question forms colourless tabular crystals, which are decomposed by water, with formation of sulphuric acid and arsenious anhydride. Compounds of As_2O_3 with 1, 2, 4, and 8 SO_3 are known.

Antimony (stibium), Sb = 120,[39] is another analogue of phosphorus. In its external appearance and the properties of its compounds it resembles the metals still more closely than arsenic. In fact, antimony has the appearance, lustre, and many of the characteristic properties of the metals. Its oxide, Sb_2O_3, already shows the earthy appearance of rust or of lime, and has distinctly basic properties, although it corresponds with nitrous and phosphorous anhydride, and is able, like them, to give saline compounds with bases. At the same time, antimony presents, in the majority of its compounds, an entire analogy with phosphorus and arsenic. Its compounds belong to the type, SbX_3 and SbX_5. It is found in nature, chiefly in the form of sulphide, Sb_2S_3. This substance sometimes occurs in large masses in mineral veins, and is known in mineralogy under the name of antimony glance, or *stibnite*, and in trade as *antimony*. Besides which antimony partially or totally replaces arsenic in some minerals ; thus, for example, a compound of antimony sulphide and arsenic sulphide with silver sulphide is found in red silver ore. But in every case antimony is a rather rare metal found in few localities. It is extracted chiefly for the preparation of alloys with lead and tin, which are used for casting printing type. Some of its compounds are also used in medicine, the most important in this respect being antimony pentasulphide, Sb_2S_5 (*sulfur auratum antimonii*), and tartar emetic, which is a double salt derived from tartaric acid and has the composition, $C_4H_4K(SbO)O_6$. Even the native antimony sulphide is

even in very small quantities—several centigrammes. It is all the more remarkable that the inhabitants of certain mountainous countries accustom themselves to taking arsenic, as a means which, from their experience, helps to overcome the fatigue of mountain ascents. Arsenious anhydride and certain of its salts are also used in medicine, only naturally in small quantities. When taken internally arsenic passes into the blood, and is mainly excreted by the urine, in which it may be recognised for some length of time after it has been taken, if the amount of arsenic taken has not produced those inflammatory symptoms which form the main cause of death from arsenic poisoning as from other similar mineral poisons.

[39] This atomic weight was determined by Cooke.

used in large quantities as a purgative for horses and dogs. Metallic antimony is extracted from the glance, Sb_2S_3, by roasting, when the sulphur burns away and the antimony oxidises, forming the oxide Sb_2O_3, which is then heated with charcoal, and thus reduced to a *metallic state*. The reduction may be carried on in the laboratory on a small scale, by fusing the sulphide with iron, which takes up the sulphur.[40]

Metallic antimony has a white colour and a brilliant lustre, which remains untarnished in the air, because the metal does not oxidise at the ordinary temperature. It crystallises in rhombohedra, and always shows a distinctly crystalline structure, which gives it quite a different aspect from the majority of the metals yet known. It is most like tellurium in this respect. Antimony is brittle, so that it is very easily converted into a powder; its specific gravity is 6·7, it melts at about 432°, but only volatilises at a bright red heat. When heated in the air—for instance, before the blow-pipe—it burns and gives white odourless fumes, consisting of the oxide. This oxide is termed antimonious oxide, although it might as well be termed antimonious anhydride. It is given the first name because in the majority of cases its compounds with acids are used, but it forms compounds with the alkalis just as easily.

Antimonious oxide, like arsenious anhydride, crystallises either in regular octahedra or in rhombic prisms; its sp. gr. is 5·56; when heated it becomes yellow and then fuses, and when further heated in air it oxidises, forming an oxide of the composition Sb_2O_4. Antimonious oxide is insoluble in water and in nitric acid, but it easily dissolves in strong hydrochloric acid and in alkalis, as well as in tartaric acid or solutions of its acid salts. When dissolved in the latter it forms tartar emetic. It is precipitated from its solutions in alkalis and acids (by the action of acids on the former and alkalis on the latter) in an anhydrous form and not as hydrate. It occurs native but rarely. As a base it gives salts of the type, SbOX (as if the basic salts=SbX_3,Sb_2O_3) and hardly ever forms salts, SbX_3. In the antimonyl salts, SbOX, the group SbO is univalent, like potassium or silver. The oxide itself is $(SbO)_2O$, the hydroxide, SbO(OH), &c.; tartar emetic is a salt in which one hydrogen of tartaric acid is replaced by potassium and the other by

[40] Antimony is prepared in a state of greater purity by heating with charcoal the oxide obtained by the action of nitric acid on the impure commercial metallic antimony. This is based on the fact that by the action of the acid, antimony forms the oxide Sb_2O_5, which is but slightly soluble in water. The arsenic, which is nearly always present, forms soluble arsenious and arsenic acids, and remains in solution. The purest antimony is easily obtained from tartar emetic, by heating it with a small quantity of nitre. Metallic antimony also occurs, although rarely, native; and as it is very easily obtained, it was known to the alchemists of the fifteenth century. Very pure metallic antimony may be deposited by the electric current from a solution of antimonious sulphide in sodium sulphide after the addition of sodium chloride to the solution.

antimonyl, SbO. Antimonious oxide is very easily separated from its salts by any base, but it must be observed that this separation does not take place in the presence of tartaric acid, owing to the property of tartaric acid of forming a soluble double salt—*i.e.* tartar emetic.[41]

If metallic antimony, or antimonious oxide, be oxidised by an excess of nitric acid and the resultant mass be carefully evaporated to dryness, then *metantimonic acid*, $SbHO_3$, is formed. Its corresponding potassium salt, $2SbKO_3,5H_2O$, is prepared by fusing metallic antimony with one-fourth of its weight of nitre and washing the resultant mass with cold water. This potassium salt is only slightly soluble in water (in 50 parts) and the sodium salt is still less so. An ortho-acid, SbH_3O_4, also appears to exist; it is obtained by the action of water on antimony pentachloride, but it is very unstable, like the pentachloride, $SbCl_5$, itself, which easily gives up Cl_2, leaving antimony trichloride, $SbCl_3$, which is decomposed by water, forming an oxychloride—for example, SbOCl, only slightly soluble in water. When antimonic acid is heated to an incipient red heat, it parts with water and forms the anhydride, Sb_2O_5, of a yellow colour and sp. gr. 6·5.[42]

[41] As antimonious oxide answers to the type SbX_3, it is evident that compounds may exist in which antimony will replace three atoms of hydrogen; such compounds have been to some extent obtained, but they are easily converted by water into substances corresponding with the ordinary formulæ of the compounds of antimony. Thus tartar emetic, $C_4H_4(SbO)KO_6$, loses water when heated, and forms $C_4H_2SbKO_6$—that is, tartaric acid, $C_4H_6O_6$, in which one atom of hydrogen is replaced by potassium and three by antimony. But this substance is re-converted into tartar emetic by the action of water.

A similar compound is seen in that *intermediate oxide of antimony* which is formed when antimonious oxide is heated in air: its composition is SbO_2 or Sb_2O_4. This oxide may be regarded as orthantimonic acid, $SbO(HO)_3$, in which three atoms of hydrogen are replaced by antimony in that state in which it occurs in oxide of antimony—*i.e.* $SbO(SbO_3) = Sb_2O_4$. This supposition clearly explains the existence of this most stable oxide of antimony, which is also formed when antimonic acid is ignited; it then loses water and oxygen, and gives this intermediate oxide as a white infusible powder, of sp. gr. 6·7. It is somewhat soluble in water, and gives a solution which turns litmus paper red.

[42] Among the other compounds of antimony, *antimoniuretted hydrogen*, SbH_3, resembles arseniuretted hydrogen in its mode of formation and properties (when liquefied, it boils at −65°, solidifies at −92°), whilst the halogen compounds differ in many respects from those of arsenic. When chlorine is passed over an excess of antimony powder, it forms *antimony trichloride*, $SbCl_3$, but if the chlorine be in excess it forms the *pentachloride*, $SbCl_5$. The trichloride is a crystalline substance which melts at 72°, and distils at 230°, whilst the pentachloride is a yellow liquid, which splits up into chlorine and the trichloride when heated; at 140° it begins to give off chlorine abundantly, carrying away the vapour of the trichloride with it; and at 200° the decomposition is complete, and pure antimonious chloride only passes over. This property of antimony pentachloride has caused it to be applied in many cases for the transference of chlorine; all the more that when it has given up its chlorine, it leaves the trichloride, which is able to absorb a fresh amount of chlorine; and therefore many substances which are unable to react directly with gaseous chlorine do so with antimony pentachloride, and in the presence of a small quantity of it chlorine will act on them, just as oxygen is able, in the presence of nitrogen oxides, to oxidise substances which could not be oxidised at the

The heaviest analogue of nitrogen and phosphorus is *bismuth*, Bi = 208. Here, as in the other groups, the basic, metallic properties increase with the atomic weight. Bismuth does not give any hydrogen compound, and the highest oxide, Bi_2O_5, is a very feeble acid oxide. Bismuthous oxide, Bi_2O_3, is a base, and bismuth itself a perfect metal. To explain the other properties of bismuth it must further be remarked that in the eleventh series it follows mercury, thallium, and lead, whose atomic weights are near to that of bismuth, and that therefore it resembles them and more especially its nearest neighbour, lead. Although PbO and PbO_2 represent different types from Bi_2O_3 and Bi_2O_5, they resemble them in many respects, even in their external appearance, and especially in their mutual compounds, the lower basic and the higher acid, which easily evolve oxygen. But judging by the formula, Bi_2O_3 is a more feeble base than PbO. They both easily give basic salts.

This gives nearly the whole history of the compounds of bismuth. Thus *bismuth* forms compounds of two types BiX_3 and BiX_5,[43] which

expense of free oxygen. Thus carbon bisulphide is not acted on by chlorine at low temperatures—this reaction requires a high temperature—but in the presence of antimony pentachloride its conversion into carbon tetrachloride takes place at low temperatures. Antimony tri- and pentachloride, having the character of chloranhydrides, fume in air, attract moisture, and are decomposed by water, forming antimonious and antimonic acids. But in the first action of water the trichloride does not evolve all its chlorine as hydrochloric acid, which is understood from the fact that antimonious anhydride is also a base; it is therefore able to react on acids, and indeed even antimony sulphide dissolved in an excess of hydrochloric acid (hydrogen sulphide is evolved) gives an aqueous solution of antimony trichloride, which, when carefully distilled, even gives the anhydrous compound. Antimony trichloride is only decomposed by an excess of water, and then not completely, for with a large mass of water it forms *powder of algaroth—i.e.* antimony oxychloride. The first action of water consists in the formation of *oxychloride*, SbOCl—that is, a salt corresponding to oxide of antimony as a base. If antimony oxide or antimony chloride be dissolved in an excess of hydrochloric acid, and the solution diluted with a considerable amount of water, then this same powder of algaroth is precipitated. The composition varies with the relative amount of water; namely, between the limits SbOCl and $Sb_4O_5Cl_2$. The latter compound is, as it were, a basic salt of the former, because its composition = $2(SbOCl)Sb_2O_3$.

With bromine and iodine, antimony forms compounds similar to those with chlorine. Antimonious bromide, $SbBr_3$, crystallises in colourless prisms, melts at 94°, and boils at 270°; antimonious iodide, SbI_3, forms red crystals of sp. gr. 5·0; antimony trifluoride, SbF_3, separates from a solution of antimonious oxide in hydrofluoric acid, and SbF_5 is formed by a similar treatment of antimonic acid. The latter gives easily-soluble double salts with the fluoride of the metals of the alkalis.

De Haën (1887) obtained very stable double soluble salts, SbF_3,KCl (100 parts of water dissolve 57 parts of salt), SbF_3,K_2SO_4, &c., which he proposed to make use of in the arts as very easily crystallisable and soluble salts of antimony.

Engel, by passing hydrochloric acid gas into a saturated solution of antimonious chloride at 0°, obtained a compound $HCl,2SbCl_3,2H_2O$, and with the pentachloride a compound $SbCl_5,5HCl,10H_2O$. Bismuth trichloride, $BiCl_3$, gives a similar compound.

[43] Metallic bismuth is very easily obtained when the compounds of the oxide are

entirely recall the two types which we have already seen for the compounds of lead. Just as in the case of lead, the type PbX_2 is basic, stable, as a rule easily formed, and passes with difficulty into the higher and lower types, which are unstable, so also in the case of bismuth the type of combination BiX_3 is the usual basic form. The higher type of combination BiX_5,[44] in fact, behaves towards this stable type BiX_3 in exactly the same manner as lead dioxide does to the monoxide; and bismuthic acid is obtained by the action of chlorine on bismuth oxide shaken in water, in exactly the same way as lead dioxide is obtained from lead oxide. It is an oxidising agent, like lead dioxide, and even the acid character in bismuthic acid is only slightly more developed than in lead dioxide. Here, as in the case of lead (minium), intermediate compounds are easily formed, in which the bismuth of the lower oxide plays the part of a base combined with the acid which is formed by the higher form of the oxidation of bismuth. In this resemblance of the neighbouring elements, Bi = 208 and Pb = 206, of different groups, we find the explanation of many facts of chemistry, and we see in them the naturalness of the periodic system of the elements.

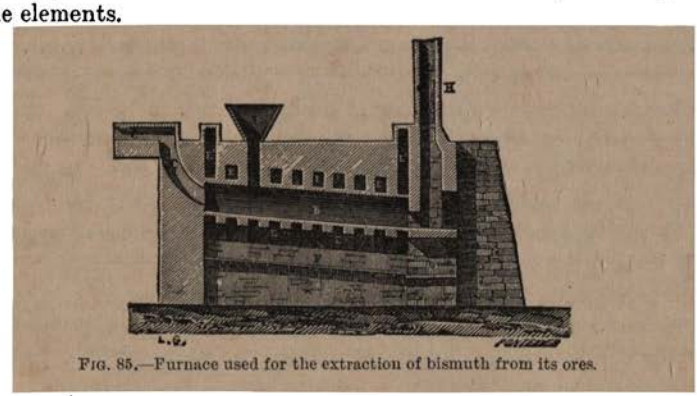

FIG. 85.—Furnace used for the extraction of bismuth from its ores.

In nature, bismuth occurs in only a few localities and in small quantities, most frequently in a native state, and more rarely as oxide and as a compound of bismuth sulphide with the sulphides of other metals. It is extracted from its ores by simple fusion in the furnace shown in fig. 85. This furnace contains an inclined iron retort, into

reduced by powerful reducing agents, but when less powerful reducing agents—for example, stannous oxide—are taken, then bismuth suboxide is formed as a black crystalline powder. It is a compound of the type BiX_2, its composition being BiO; it is decomposed by acids into the metal and oxide, which passes into solution.

[44] The type BiX_5 is represented by the pentoxide, Bi_2O_5, its metahydrate, Bi_2O_5,H_2O, or $BiHO_3$, known as bismuthic acid, and the pyrohydrate, $Bi_2H_4O_7$. *Bismuth pentoxide* is obtained by the prolonged passage of chlorine through a boiling solution of

the upper extremity of which the ore is charged, and the molten *metal* flows from the lower extremity. It is refined by re-melting, and the pure metal may be obtained by dissolving in nitric acid, decomposing the resultant salt with water, and reducing the precipitate by heating it with charcoal. Bismuth is a metal which crystallises very well from a molten state. Its sp. gr. is 9·8; it melts at 268°, and if it be melted in a crucible, allowed to slowly cool, and the crust broken and the remaining molten liquid poured out, perfect rhombohedral crystals of bismuth are obtained on the sides of the crucible. It is brittle, has a grey-coloured fracture with a reddish lustre, is not hard, and is but very slightly ductile and malleable; it volatilises at a white heat and easily oxidises. It recalls antimony and lead in many of its properties. When oxidised in air, or when the nitrate is ignited, bismuth forms the *oxide* Bi_2O_3 as a white powder, which fuses when heated and resembles massicot. The addition of an excess of caustic potash to a solution of a bismuthous salt gives a white precipitate of the hydroxide, BiO(OH), which loses its water and gives the anhydrous oxide when boiled with a solution of caustic potash. Both the hydroxide and oxide easily dissolve in acids, and form bismuthous salts.

Bismuthous oxide, Bi_2O_3, is a feeble and unenergetic base. The normal hydroxide of the oxide Bi_2O_3 is $Bi(OH)_3$; it parts with water and forms a metahydroxide (bismuthyl hydroxide), BiO(OH). Both of these hydroxides have their corresponding saline compounds of the composition BiX_3 and BiOX. And the form BiOX is nothing else but the type of the basic salt, because $3ROX = RX + R_2O_3$. It is evident that in the type BiX_3 the bismuth replaces three atoms of hydrogen. And, indeed, with phosphoric acid, solutions of the bismuthous salts give a precipitate of the composition $BiPO_4$. On the other hand, in the form of compounds BiOX or $Bi(OH)_2X$, the univalent group (BiO) or (BiH_2O_2) is combined with X. Many bismuth salts are formed according to the type BiOX. For instance, the carbonate $(BiO)_2CO_3$, which corresponds with the other carbonates M_2CO_3. It is obtained as a white precipitate when a solution of sodium carbonate is added to

potassium hydroxide (sp. gr. 1·38), containing bismuth oxide in suspension; the precipitate is washed with water, boiling nitric acid (but not long, as otherwise the bismuthic acid is decomposed), then again with water, and then the resultant bright red powder of the hydrate $BiHO_3$ is dried at 125°. The prolonged action of nitric acid on bismuthic anhydride, Bi_2O_5, results in the formation of the compound Bi_2O_4,H_2O, which decomposes in moist air, forming Bi_2O_3. The density of bismuthic anhydride is 5·10, of the tetroxide, Bi_2O_4, 5·60, and of bismuthic acid, $BiHO_3$, 5·75. *Pyrobismuthic acid*, $Bi_2H_4O_7$, forms a brown powder, which loses a portion of its water at 150°, and decomposes on further heating, with the evolution of oxygen and water. It is obtained by the action of potassium cyanide on a solution of bismuth nitrate.

a solution of a bismuth salt.[45] The complex radicle BiO is naturally not any particular special grouping, as was represented in former times in speaking of complex radicles; it is simply only a form of expression of the composition of a given oxide according to its relation to the compounds of other oxides.

Three *salts of nitric acid* are known corresponding with bismuthous oxide. If metallic bismuth or its oxide be dissolved in nitric acid, it forms a colourless, transparent solution, containing a salt, which separates in large transparent crystals containing $Bi(NO_3)_3,5H_2O$. When heated at 80°, these crystals melt in their water of crystallisation, and in so doing lose a portion of their nitric acid, together with water, forming a salt whose empirical formula is $Bi_2N_2H_2O_9$. If the preceding salt belongs to the type BiX_3, then this one should belong to the form BiOX, because it contains one equivalent of the radicle of nitric acid, NO_3, per one equivalent of bismuth, and one is led to suppose that this salt has a composition $Bi(OH)_2NO_3$ in combination with $BiO(NO_3)$. This salt may be heated to 150° without change. When the first colourless crystalline salt dissolves in water *it is decomposed.* There is no decomposition if an excess of acid be added to the water—that is to say, the salt is able to exist in an acid solution without decomposing, without separation of the so-called basic salt—but by itself it cannot be kept in solution; water decomposes this salt, acts on it like an alkali. Hence the basic properties of bismuthic oxide are so feeble that even water, with its at all events little developed alkaline properties, acts by taking up a portion of the acid from it. Here we see one of the most striking facts, long since observed, confirming that action of water on salts about which we have spoken in Vol. I. p. 426 and elsewhere. This action of water may be expressed thus :—$BiX_3 + 2H_2O = Bi(OH)_2X + 2XH$. A salt of the type BiX_3 is decomposed by an excess of water, and a salt of the type $Bi(OH)_2X$ is obtained in the precipitate. But if the quantity of acid, HX, be increased, then the salt BiX_3 is again formed and passes into solution. The quantity of the salt BiOX which passes into solution on the addition of a given quantity of acid depends indubitably on the amount of water (Muir). The solution, which is perfectly transparent with a small amount of water, becomes cloudy and separates out the salt of the type BiOX, when diluted. The white flaky precipitate of $Bi(OH)_2NO_3$ formed from the normal salt $Bi(NO_3)_3$ by mixing it with five parts of water, and in general with a small amount of water, is used in medicine under the name of magistery of bismuth.[46]

[45] Basic bismuth carbonate is employed for whitening the skin (veloutine, &c.).

[46] With an excess of water a further quantity of acid is separated and a still more basi

Metallic bismuth is used for solders and in the preparation of fusible alloys. The addition of bismuth to many metals renders them very hard, and at the same time generally lowers their melting point to a considerable extent. Thus Wood's metal, which contains one part of cadmium, one part of tin, two parts of lead, and four parts of bismuth, fuses at about 60°, and in general many alloys composed of bismuth, tin, lead, and antimony melt below or about the boiling-point of water.[47]

Just as in the II. group, besides the elements zinc, cadmium, and mercury in the uneven series, we saw calcium, strontium, and barium in the even series; and as in the IV. group, besides *silicon*, germanium, tin, and lead, we saw thallium, zirconium, cerium, and *thorium*; so also in the V. group we find, besides those elements of the uneven series just considered by us, a series of analogues in the even series, which, with a certain degree of similarity (mainly quantitative, or relative to the atomic weights), also present a series of particular (qualitative) independent points of distinction. In the even series are known *vanadium*, which stands between titanium and chromium, *niobium*, between zirconium and molybdenum, and *tantalum*, situated near

salt formed. The ultimate product, on which an excess of water has apparently no action whatever, is a substance having the composition $BiO(NO_3),BiO(OH)$. In the latter salts we already see the limit of change, and this limit appears to show that the form of the saline compound of bismuthic oxide are of the forms Bi_2X_6, and not BiX_5, and it is very probable, on the basis of the examples which we considered in the case of lead, that this type should be still further polymerised in order to have an idea of the type of the bismuthous compounds. If we refer all the bismuthous compounds to this type, Bi_2X_6, we shall obtain the following expression for the composition of the nitrates: normal salt, $Bi_2(NO_3)_6$, first basic salt, $Bi_2O(OH)_2(NO_3)_2$, magistery of bismuth, $Bi_2(OH)_4(NO_3)_2$, and the limiting form $Bi_2O_2(OH)(NO_3)$.

The character of bismuthous oxide in its compounds is clearly seen in the example of the nitrate, because, for example, bismuthous chloride, $BiCl_3$, which is obtained by heating bismuth in chlorine, or by dissolving it in aqua regia, and then distilling without the access of air, is also decomposed by water in exactly the same manner, and forms basic salts—for instance, first, BiOCl, like the above salt of nitric acid. Bismuth chloride is volatile, and perhaps its formula is $BiCl_3$, and not Bi_2Cl_6. Polymerisation may take place in some compounds and not in others. A volatile compound of the composition $Bi(C_2H_3)_3$ is also known as a liquid which is insoluble in water and decomposes with explosion when heated to 130°.

[47] As the metals contained in alloys like the above (bismuth, lead, tin, cadmium) are difficultly volatile and their alloys are fusible, they may be employed in the place of mercury in many physical experiments conducted at 70° and above, and they offer the advantage that they do not give any vapour having a tension (mercury at 100°, 0·75 mm.). These alloys may, for example, be used in thermometers, manometers, baths, &c. It must, however, be borne in mind that in solidifying they expand, and glass vessels in which they have solidified always break after a certain time. Bismuth expands in passing into a molten state, but it has a temperature of maximum density. According to Luedeking the mean coefficient of expansion of liquid bismuth is 0·0000442 (between 270° and 308°), and of solid bismuth 0·0000411.

tungsten, an element of the VI. group, like chromium and molybdenum. Just as bismuth is similar in many respects to its neighbour lead, so also do these neighbouring elements resemble each other, even in their external appearance, not to mention the quality of their compounds, naturally taking into account the difference of the types corresponding with the different groups. The occurrence in the V. group determines the types of the oxides R_2O_3 and R_2O_5, and the development of an acid character in the higher oxides. The occurrence in the even series determines the absence of volatile compounds, RH_3, for these metals, and a more basic character of the oxides of a given composition than in the uneven series, &c.[48] Vanadium, niobium, and tantalum belong to the number of rare metals, and are exceedingly difficult to obtain pure, more especially owing to their similarity to and occurrence with chromium, tungsten, and other metals, and also in combination among themselves; therefore it is natural that they have been far from completely studied, although since 1860 chemists have devoted not a little time to the investigation of these elements. The researches carried out by Marignac, of Geneva, on niobium, and by Sir Henry Roscoe, of Manchester, on vanadium, deserve special attention. The undoubted external resemblance between the compounds of chromium and vanadium, as well as the want of completeness in the knowledge of the compounds of vanadium, long caused its oxides to be considered analogous in atomic composition with those formed by chromium. The higher oxide of vanadium was therefore supposed to have the formula VO_3. But the fact of the matter is, that the chemical analogy of the elements does not proceed in one direction only; vanadium is at one and the same time the analogue of chromium, and consequently of the elements like sulphur of the VI. group, and also the analogue of phosphorus, arsenic, and antimony; just as bismuth stands in respect to lead and antimony. Investigation has shown that the compounds of vanadium are always accompanied by those of phosphorus as well as of iron, and that it is even more difficult to separate it from the compounds of phosphorus than from those of iron and tungsten. We should have to considerably extend our description if we wished to give the complete history, even of vanadium alone, not to mention niobium and tantalum, all the more as not unfrequently many questions concerning the compounds of these elements have not yet been fully explained. Therefore we shall limit ourselves to pointing out the

[48] Although, guided by Brauner, who showed that didymium gives a higher oxide, Di_2O_5, I place this element in the fifth group, still I am not certain as to its position, because I consider that the questions bearing on this metal are still far from being definitely answered.

most important points in the history of this element, all the more as the very minerals in which these elements occur are excessively rare and accessible to only a few investigators.

An important point in the history of the members of this group is seen in the circumstance that they form volatile compounds with chlorine, similar to the like compounds of the elements of the phosphorus group, namely, of the type RX_5, or one corresponding to it. The vapour densities of the compounds of this nature were determined, and served as the most important basis for the explanation of the atomic composition of these molecules. In this we see the power of those general and fundamental laws, like the law of Avogadro-Gerhardt. An oxychloride, $VOCl_3$, is known for vanadium, which is the perfect analogue of phosphorus oxychloride. It was formerly considered to be vanadium chloride, for exactly the same story was repeated over vanadium as over uranium (Chapter XXI.); its lower oxide, VO, was considered to be the metal, because it is exceedingly difficultly reduced—even potassium does not remove all the oxygen, besides which it has a metallic appearance, and decomposes acids like a metal; in a word, it in every respect resembles a metal. *Vanadium oxychloride* is obtained by heating the trioxide, V_2O_3, mixed with charcoal, in a current of hydrogen; the lower oxide of vanadium is then formed, and it, when heated in a current of dry chlorine, gives the oxychloride $VOCl_2$ as a reddish liquid, which does not act on sodium, and may be purified by distillation over this metal. It fumes in the air, forming reddish fumes; it reacts on water, forming hydrochloric and vanadic acids; hence, on the one hand it is very similar to phosphorus oxychloride, and on the other hand to chromium oxychloride, CrO_2Cl_2 (Chapter XXI.). It is of a yellow colour, its sp. gr. is 1·83, it boils at 120°, and its vapour density is 86 with respect to hydrogen, and therefore the above formula expresses its molecular weight.[49]

Vanadic anhydride, V_2O_5, is obtained either in small quantities from certain clays where it accompanies the oxides of iron (hence some sorts of iron contain vanadium) and phosphoric acid, or from the rare

[49] When the vapours of vanadium oxychloride are heated together with zinc in a closed tube at 400°, they lose a portion of their chlorine and form a green crystalline mass of sp. gr. 2·88, which is deliquescent in air and has the composition $VOCl_2$. Only its vapour density is unknown, and it would be extremely important to determine whether its molecular composition is that given above, or if it corresponds with the formula $V_2O_2Cl_4$. Another less volatile oxychloride, VOCl, is formed together with it as a brown insoluble substance, which is, however, soluble in nitric acid like the preceding. Roscoe obtained even a still less chlorinated substance, namely, $(VO)_2Cl$; but it may only consist of a mixture of VO and VOCl. At all events, we here find such a graduated series as is met with for very few other elements.

minerals: *volborthite*, $CuHVO_4$, or basic vanadate of copper; *vanadinite*, $PbCl_2 3Pb_3(VO_4)_2$; lead vanadate, $Pb_3(VO)_{42}$, &c. The latter salts are carefully ignited for some time with one-third of their weight of nitre; the fused mass thus formed is powdered and boiled in water: the yellow solution obtained contains potassium vanadate. The solution is neutralised with acid, and barium chloride added; a meta-salt, $Ba(VO_3)_2$, is then precipitated as an almost insoluble white powder, which gives a solution of vanadic acid when boiled with sulphuric acid. (The precipitate is at first yellow, as long as it remains amorphous, but it afterwards becomes crystalline and white.) The solution thus obtained is neutralised with ammonia, which thus forms ammonium (meta) vanadate, NH_4VO_3, which, when evaporated, gives colourless crystals, insoluble in water, containing sal-ammoniac; hence this salt is precipitated by adding a piece of sal-ammoniac to the solution. Ammonium vanadate, when ignited, leaves vanadic acid behind. In this it differs from the corresponding chromium salt, which is deoxidised into chromium oxide when ignited. In general, vanadic acid has but a small oxidising action. It is reduced with difficulty, like phosphoric or sulphuric acid, and in this differs from arsenic and chromic acids. Vanadic acid, like chromic acid, separates from its solution as the anhydride V_2O_5, and not in a hydrous state. Vanadic anhydride, V_2O_5, forms a reddish brown mass, which easily fuses and solidifies into transparent crystals having a violet lustre (another point of resemblance to chromic acid), and dissolves in water, forming a yellow solution with a slightly acid reaction.[50]

[50] Strong acids and alkalis dissolve vanadic anhydride in considerable quantities, forming yellow solutions. When it is ignited, especially in a current of hydrogen, it evolves oxygen and forms the lower oxides; V_2O_4 (acid solutions of a green colour, like the salts of chromic oxide), V_2O_3, and the lowest oxide, VO. The latter is the metallic powder which is obtained when the vanadium oxychloride is heated in an excess of hydrogen, and was formerly mistaken for metallic vanadium. When a solution of vanadic acid is treated with metallic zinc it forms a blue solution, which seems to contain this oxide. It acts as a reducing agent (and forms an intimate analogue to chromous oxide, CrO). Metallic *vanadium* can only be obtained from vanadium chloride, which is quite free from oxygen. The specific gravity of this metal is 5·5. It is of a grey-white colour, is not decomposed by water, is not oxidised in air, but burns when strongly heated, and can be fused in a current of hydrogen. It is insoluble in hydrochloric acid, but easily dissolves in nitric acid, and when fused with caustic soda it forms sodium vanadate.

As regards the salts of vanadic acid, three different classes of salts are known; the first correspond with metavanadic acid, $VMO_3 = M_2OV_2O_5$, the second correspond with the dichromates—that is, have the composition $V_4M_2O_{11}$, which is equal to $M_2O + 2V_2O_5$—and the third correspond with orthovanadic acid, VM_3O_4 or $3M_2O + V_2O_5$. The latter are formed when vanadic anhydride is fused with an excess of an alkaline carbonate. A fourth type of salts is also known corresponding with the trichromates, and having the composition $M_2V_6O_{16} = M_2O + 3V_2O_5$. The latter are formed by the metals of the alkalis and have the appearance of red crystals, resembling chromates. They are formed from

Niobium and tantalum occur as acids in rare minerals, and are mainly extracted from *tantalite* and *columbite*, which are found in Bavaria, Finland, North America, and in the Urals. These minerals are composed of the ferrous salts of niobic and tantalic acids; they contain about 15 per cent. of ferrous oxide in isomorphous mixture with manganous oxide, in combination with various relative amounts of tantalic and niobic anhydrides. These minerals are first fused with a considerable amount of potassium bisulphate, and the fused mass is boiled in water, which dissolves the ferrous salt and leaves an insoluble residue of impure niobic and tantalic acids, &c. This raw product is then treated with ammonium sulphide, in order to extract the tin and tungsten, which pass into solution. The residue containing the acids (according to Marignac) is then treated with hydrofluoric acid, in which it entirely dissolves, and potassium fluoride is added to the resultant hot solution; on cooling, a sparingly-soluble double fluoride of potassium and tantalum separates out in fine crystals, while the much more soluble niobium salt remains in solution. The difference in the solubility of these double salts in water acidified with hydrofluoric acid (in pure water the solution becomes cloudy after a certain time) is so great that the tantalum compound requires 150 parts

the bivanadates by the action of a solution of acetic acid; hence they in this respect also resemble many chromates, which are also formed directly by the removal of an alkali by an acid, although it would be nitric and not acetic acid.

Vanadium was discovered at the beginning of this century by Del-Rio, and afterwards investigated by Sefström, but it was only in 1868 that Roscoe established the above formulæ of the vanadic compounds. The researches made by Roscoe were preceded by those of Marignac in 1865, on the *compounds* of *niobium* and *tantalum*, to which were also ascribed different formulæ from those now recognised. Tantalum was discovered simultaneously with vanadium by Hatchett and Ekeberg, and was afterwards studied by Rose, who in 1844 discovered niobium in it. Notwithstanding the numerous researches of Hermann (in Moscow), Kobell, Rose, and Marignac, still there is not yet any certainty as to the purity of, and the results obtained for, the compounds of these elements. They are difficult to separate from each other, and especially from the cerite metals and titanium, &c., which accompany them. Before the investigations of Rose the highest oxide of tantalum was supposed to belong to the type TaX_6—that is, its composition was taken as TaO_5, and to the lower oxide was ascribed a formula TaO_2. Rose gave the formula TaO_2 to the higher oxide, and discovered a new element called niobium in the substance previously supposed to be the lower oxide. He even admitted the existence of a third element occurring together with tantalum and niobium, which he named pelopium, but he afterwards found that pelopic acid was only another oxide of niobium, and he considered it probable that the higher oxide of this element is NbO_2, and the lower Nb_2O_5. Hermann found that niobic acid which was considered pure contained a considerable quantity of tantalic acid, and besides this he admitted the existence of another special metallic acid, which he called ilmenic acid, after the locality (the Ilmen mountains of the Urals) of the mineral from which he obtained it. V. Kobell recognised still another acid, which he called dianic acid, and these different testimonies were only brought in agreement in the sixties by Marignac. He first of all indicated an accurate method for the separation of tantalic and niobic compounds, which are always obtained in admixture.

of water for its solution, and the niobium compound only requires 13 parts of water. The Greenland columbite (sp. gr. 5·36) only contains niobic acid, and that from Bodenmais (Bavaria, sp. gr. 6·06) almost equal quantities of tantalic and niobic acids. Having isolated tantalic and niobic salts, Marignac found that the relation between the potassium and fluorine in them is very variable—that is, that there exist various double salts of fluoride of potassium, and of the fluorides of the metals of this group, but that with an excess of hydrofluoric acid both the tantalum and niobium compounds contain seven atoms of fluorine to two of potassium, whence it must be concluded that the simplest formula for these double salts will be $K_2RF_7 = RF_5, 2KF$—that is, that the type of the higher compounds of niobium and tantalum is RX_5, and hence is similar to phosphoric acid. A chloride $TaCl_5$ may be obtained from pure tantalic acid by heating it with charcoal in a current of chlorine. This is a yellow crystalline substance, which melts at 211°, and boils at 241°; its vapour density with respect to hydrogen is 180, as would follow from the formula $TaCl_5$. It is completely decomposed by water into tantalic and hydrochloric acids. *Niobium pentachloride* may be prepared in the same manner; it fuses at 194°, and boils at 240°. When treated with water this substance gives a solution containing niobic acid, which only separates out on boiling the solution. Delafontaine and Deville found its vapour density to be 9·3.[51]

[51] If niobic acid be mixed with a small quantity of charcoal and ignited in a stream of chlorine, then a difficultly-fusible and difficultly-volatile oxychloride, $NbOCl_3$, separates. The vapour density of this compound with respect to air is 7·5, and this vapour density gives a perfect certainty to the accuracy of the formulæ given by Marignac, and shows the quantitative analogy between the compounds of niobium and tantalum, and those of phosphorus and arsenic, and consequently also of vanadium. In their qualitative relations (as is seen from the correspondence of the atomic weights also), the compounds of tantalum and niobium exhibit a great analogy with the compounds of molybdenum and tungsten. Thus zinc, when acting on acid solutions of tantalic and niobic compounds, gives a blue coloration, exactly as it does with those of tungsten and molybdenum (titanium also). These acids form the same large number of salts as those of tungsten and molybdenum. The anhydrides of the acids are also insoluble in water, but as colloids are sometimes held in solution, just like those of titanic and molybdic acids. Furthermore, niobium is in every respect the nearest analogue of molybdenum, and tantalum of tungsten. *Niobium* is obtained by reducing the double fluoride of niobium and sodium, with sodium. It is difficult to obtain in a pure state. It is a metal on which hydrochloric acid acts with some energy, as also does hydrofluoric acid mixed with nitric acid, and also a boiling solution of caustic potash. *Tantalum*, which is obtained in exactly the same way, is a much heavier metal. It is infusible, and is only acted on by a mixture of hydrofluoric and nitric acids. Rose in 1868 showed that in the reduction of the double fluoride, $NbF_5, 2KF$, by sodium, a greyish powder is obtained after treating with water. The specific gravity of this powder is 6·8, and he considers it to be niobium hydride, NbH. Neither did he obtain metallic niobium when he reduced with magnesium and aluminium, but an alloy Al_5Nb, having a sp. gr. of 4·5.

Niobium, as far as is known, unites in three proportions with oxygen. NbO, which is

formed when $NbOF_3,2KF$ is reduced by sodium; NbO_2, which is formed by igniting niobic acid in a stream of hydrogen, and niobic anhydride, Nb_2O_5, a white infusible substance, which is insoluble in acids, and has a specific gravity of 4·5. Tantalic anhydride closely resembles niobic anhydride, and has a specific gravity of 7·2. *The tantalates and niobates* present the type of ortho-salts—for example, $Na_2HNbO_4,6H_2O$, and also of pyro-salts, such as $K_3HNb_2O_7,6H_2O$, and of meta-salts—for example, $KNbO_3,2H_2O$. And, besides these, they give salts of a more complex type, containing a larger amount of the elements of the anhydride; thus, for instance, when niobic anhydride is fused with caustic potash it forms a salt which is soluble in water, and crystallises in monoclinic prisms, having the composition $K_8Nb_6O_{19},16H_2O$. There is a perfectly similar isomorphous salt of tantalic acid. Tantalite is a salt of the type of metatantalic acid, $Fe(TaO_3)_2$. The composition of Yttrotantalite appears to correspond with orthotantalic acid.

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CHAPTER XX

SULPHUR, SELENIUM, AND TELLURIUM

THE acid character of the higher oxides RO_3 of the elements of the VI. group is still more clearly defined than that of the higher oxides of the preceding groups, whilst feeble basic properties only appear in the oxides RO_3 of the elements of the even series, and then only for those elements having a high atomic weight—that is, under those two conditions in which, as a rule, the basic characters increase. Even the lower types RO_2 and R_2O_3, &c., formed by the elements of the VI. group, are acid anhydrides in the uneven series, and only those of the elements of the even series have the properties of peroxides or even of bases.

Sulphur is the representative of the VI. group both owing to the fact that the acid properties of the group are sharply defined in it, and also because it is more widely distributed in nature than any of the other elements belonging to this group. As an element of the uneven series of the VI. group, sulphur gives H_2S, sulphuretted hydrogen, SO_3, sulphuric anhydride, and SO_2, sulphurous anhydride. And in all of them we find acid properties—SO_3 and SO_2 are anhydrides of acids, and H_2S is an acid, although a feeble one. As an element sulphur has all the properties of a true non-metal; it has not a metallic lustre, does not conduct electricity, is a bad conductor of heat, is transparent, and combines directly with metals—in fact, all the properties of the non-metals, like oxygen and chlorine. Furthermore, sulphur exhibits a great qualitative and quantitative *resemblance to oxygen*, especially from the fact that it, like oxygen, combines *with two atoms of hydrogen*, and forms compounds like oxides with metals and non-metals. In this sense and aspect sulphur is bivalent, if the halogens are univalent.[1] The chemical character of sulphur is expressed by the fact

[1] The character of sulphur is very clearly defined in the organo-metallic compounds. Without lingering over this vast subject, which belongs to the province of organic chemistry, I think it will be enough for our purpose to compare the physical properties of the ethyl compounds of mercury, zinc, sulphur and oxygen. They have the common

that it forms a very slightly stable and feebly energetic acid with hydrogen, which, on the one hand, resembles water in its atomic composition, and, on the other hand, the halogen acids in its property of forming salts. The salts corresponding with this acid are the sulphides, just as the oxides correspond to water or the chlorides to hydrochloric acid. However, as we shall afterwards see more fully, the sulphides are more analogous to the former than to the latter. But although combining with metals, like oxygen, sulphur also forms chemically stable compounds with oxygen, and this fact impresses a peculiar character on all the relations of this element.[2]

Sulphur belongs to the number of those elements which *are very widely distributed in nature*, and occurs both free and combined in various forms. The atmosphere, however, is almost entirely free from compounds of sulphur, although a certain amount of them should be present, if only from the fact that sulphurous anhydride is emitted from the earth in volcanic eruptions. Sea and river water generally contain more or less sulphur in the form of sulphates. The beds of gypsum, sodium sulphate, magnesium sulphate, and the like are formations of undoubtedly aqueous origin. The sulphates contained in the soil are the source of the sulphur found in plants, and are indispensable to their growth. Among vegetable substances, the proteïds always contain from one to two per cent. of sulphur. From plants these albuminous substances, together with their sulphur, pass into the animal organism, and therefore the decomposition of animal matter is accompanied by the odour of sulphuretted hydrogen, as the product into which the sulphur passes in the decomposition of the albuminous substances. Thus a rotten egg emits sulphuretted hydrogen. Sulphur occurs largely in nature, as the various insoluble sulphides of the metals. Iron, copper, zinc, lead, antimony, arsenic, &c., occur in nature combined with sulphur. These *sulphides* frequently have a metallic lustre, and in the majority of cases occur crystallised, and also very often several sulphides occur combined or mixed together in these crystalline compounds. If they are yellow and have a metallic lustre they are called pyrites. Such are, for example,

composition $(C_2H_5)_2R$, where R = Hg, Zn, S, or O. They are all volatile: mercury ethyl, $Hg(C_2H_5)_2$, boils at 159°, its sp. gr. is 2·444, molecular volume = 106; zinc ethyl boils at 118°, sp. gr. 1·882, volume 101; ethyl sulphide, $S(C_2H_5)_2$, boils at 90°, sp. gr. 0·825, volume 107; common ether, or ethyl oxide, $O(C_2H_5)_2$, boils at 35°, sp. gr. 0·736, volume 101, in addition to which diethyl itself, $(C_2H_5)_2 = C_4H_{10}$, boils about 0°, sp. gr. about 0·62, volume about 94. Thus the substitution of Hg, S, and O scarcely changes the volume, notwithstanding the difference of the weights; the physical influence, if one may so express oneself, of these elements, which are so very different in their atomic weights, is almost alike.

[2] Therefore in former times sulphur was known as the amphid element.

copper pyrites, $CuFeS_2$, and iron pyrites, FeS_2, which is the commonest of all. They are all also known as glances or blendes if they are greyish and have a metallic lustre—for example, zinc blende, lead glance, PbS, antimony glance, Sb_2S_3, &c. And, lastly, sulphur occurs *native*. It occurs in this form in the most recent geological formations in admixture with limestone and gypsum, and most frequently in the vicinity of active or extinct volcanoes. As the gases of volcanoes contain sulphur compounds—namely, sulphuretted hydrogen and sulphurous anhydride, which by reacting on one another may produce sulphur, which also frequently appears in the craters of volcanoes as a sublimate—it might be imagined that the sulphur was of volcanic origin. But on a nearer acquaintance with its mode of occurrence, and more especially considering its relation to gypsum, $CaSO_4$, and limestone, the present general opinion leads to the conclusion that the sulphur has been formed by the reduction of the gypsum by organic matter and that its occurrence is only indirectly connected with volcanic agencies. Near Tetush, on the Volga, there are beds containing gypsum, sulphur, and asphalt (mineral tar). In Europe the most important deposits of sulphur are in the south of Sicily from Catania to Girgenti.[3] There are very rich deposits of sulphur in Daghestan near Cherkai and Cherkat in Khyut, and in the Trans-Caspian provinces; which are able to supply the whole of Russia with this mineral. Abundant deposits of sulphur have also been found in Kamtchatka in the neighbourhood of the volcanoes. The method of separation of the sulphur from its earthly impurities is based on the fact that sulphur melts when it is heated. The fusion is carried on at the expense of a portion of the sulphur, which is burnt, so that the remainder may melt and run from the mass of the earth. This is carried on in special furnaces called calcaroni.[4]

[3] When I was in Sicily, I found, near Caltanisetta, a specimen of sulphur with mineral tar. In the same neighbourhood there are naphtha springs and mud volcanoes. It may be that these substances have reduced the sulphur from gypsum.

The chief proof in favour of the origin of sulphur from gypsum is that in treating the deposits for the extraction of the sulphur it is found that the proportion between the sulphur and calcium carbonate never exceeds that which it would be had they both been derived from calcium sulphate.

[4] Naturally only those ores of sulphur which contain a considerable amount of sulphur can be treated by this method. With poor ores it is necessary to have recourse to distillation or mechanical treatment in order to separate the sulphur, but its price is so low that this is often not profitable.

The sulphur obtained by the above-described method still contains some impurities, but it is frequently made use of in this form for many purposes, and especially in considerable quantities for the manufacture of sulphuric acid, and for strewing over grapes. For other purposes, and especially in the preparation of gunpowder, a purer sulphur is required. Sulphur may be purified by distillation. The crude sulphur is called *rough*,

Sulphur is purified by distillation in special retorts (see fig. 86) by passing the vapour into a chamber G built of stone. The first portions of the vapour entering into the condensing chamber are condensed straightway from the vapour into a solid state, and form a fine powder known as *flowers of sulphur*.[5] But when the temperature of the

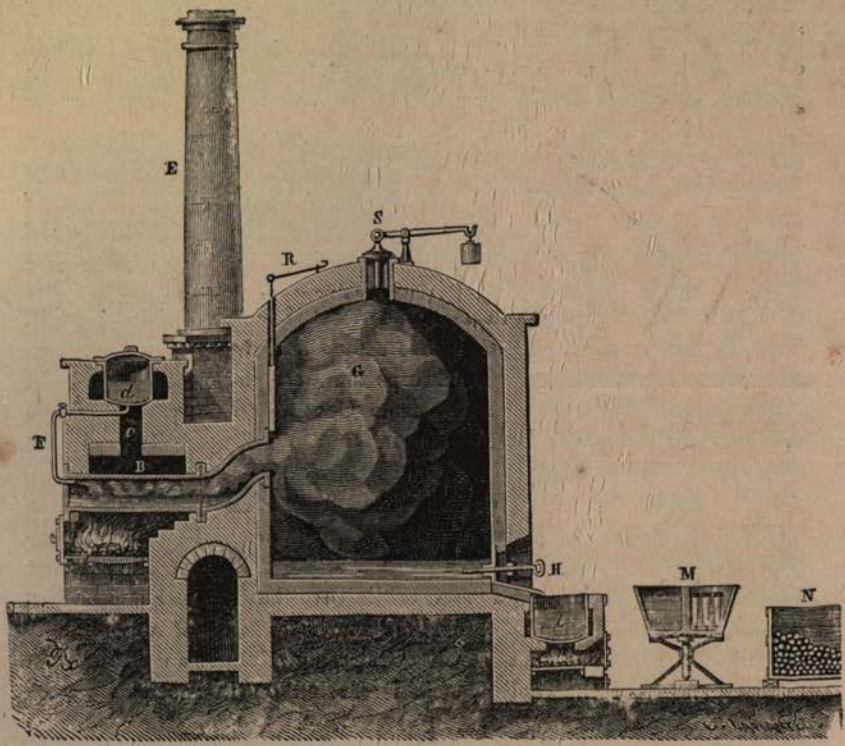


FIG. 86.—Refining sulphur by sublimation.

receiver attains the melting point of sulphur, it passes into a liquid state and is cast into moulds (like sealing wax), and it is then known under the name of *roll sulphur*.[6]

and the distilled sulphur *refined*. The arrangement given in fig. 86 is employed for refining sulphur. The rough sulphur is melted in the boiler *d*, and as it melts it is run through the tube F into an iron retort B heated by the naked flame of the furnace. Here the sulphur is converted into vapour, which passes through a wide tube into the chamber G, surrounded by stone walls and furnished with a safety-valve S.

[5] Flowers of sulphur always contains a certain amount of the oxides of sulphur.

[6] Sulphur may be extracted by various other means. It may be extracted from iron pyrites, FeS_2, which is very widely distributed in nature. From 100 parts of iron pyrites about half the sulphur contained, namely—about 25 p.c.—may be extracted by heating without the access of air, a lower sulphide of iron, which is more stable under the action

In an uncombined state sulphur exists in *several modifications*, and it forms an example of the facility with which an alteration of properties can take place without a change of composition—that is, as regards the material of a substance. Common sulphur has the well-known yellow colour. This colour fades as the temperature falls, and at $-50°$ sulphur is almost colourless. It is very brittle, so that it may be easily converted into a powder, and it presents a crystalline structure, which, by the way, shows itself in the unequal expansion of lumps of sulphur by heat. Hence when a piece of sulphur is heated by the warmth of the hand, it emits sounds and sometimes cracks, which probably also depends on the bad heat-conducting power of sulphur. It is easily obtained in a crystalline form by artificial means, because although insoluble in water it dissolves in carbon bisulphide, and in certain oils.[7] Solutions of sulphur in carbon bisulphide when evaporated at the ordinary temperature yield well-formed transparent crystals of sulphur in the form of rhombic octahedra, in which form it occurs native. The specific gravity of these crystals is 2·045. Fused sulphur, cast into moulds and cooled, has, after being kept a long time, a specific gravity 2·066 ; almost the same as that of the crystalline sulphur of the above form, which shows that common sulphur is the same as that which crystallises in octahedra. The specific heat of octahedral sulphur is 0·17 ; it melts at 114°, and forms a mobile bright yellow liquid. On further heating the fused sulphur undergoes an alteration, which we shall presently describe, first observing that the above octahedral state of sulphur is its most stable form. Sulphur may be kept at the ordi-

of heat, being left behind. Alkali waste (Vol. I. p. 514), containing calcium sulphide and gypsum, $CaSO_4$, may be used for the same purpose, but native sulphur is so cheap that recourse can only be had to these sources when the calcium sulphide appears as a worthless bye-product. The most simple process for the extraction of sulphur from alkali waste, in a chemical sense, consists in evolving sulphuretted hydrogen from the calcium sulphide by the action of hydrochloric acid. The sulphuretted hydrogen when burnt gives water and sulphurous anhydride, which reacts on fresh sulphuretted hydrogen with the separation of sulphur. The combustion of the sulphuretted hydrogen may be so conducted that a mixture of $2H_2S$ and SO_2 is straightway formed, and this mixture will deposit sulphur (Chapter XII. Note 14). Gossage and Chance treat alkali waste with carbonic anhydride, and subject the sulphuretted hydrogen evolved to incomplete combustion (this is best done by passing a mixture of sulphuretted hydrogen and air, taken in the requisite proportions, over red-hot ferric oxide), by which means water and the vapour of sulphur are formed: $H_2S + O = H_2O + S$.

[7] One hundred parts of liquid carbon bisulphide, CS_2, dissolve 16·5 parts of sulphur at $-11°$, 24 parts at 0°, 37 parts at 15°, 46 parts at 22°, and 181 parts at 55°. The saturated solution boils at 55°, whilst pure carbon bisulphide boils at 47°. The solution of sulphur in carbon bisulphide reduces the temperature, just as in the solution of salts in water. Thus the solution of 20 parts of sulphur in 50 parts of carbon bisulphide at 20° lowers the temperature by 5° ; 100 parts of benzene, C_6H_6, dissolves 0·965 parts of sulphur at 26°, and 4·377 parts at 71° ; chloroform, $CHCl_3$, dissolves 1·2 parts of sulphur at 22°, and 16·35 parts at 174°.

nary temperature in this form for an indefinite length of time, and many other modifications of sulphur pass into this form after being left for a certain time at ordinary temperature.

If sulphur be melted and then slightly cooled, so that it forms a crust on the surface and over the sides of the crucible, while the internal mass remains liquid, then the sulphur takes another crystalline form as it solidifies. This may be seen by breaking the crust, and pouring out the remaining molten sulphur.[8] It is then found that the sides of the crucible are covered with *prismatic crystals* of the monoclinic system ; they have a totally different appearance from the above-described crystals of rhombic sulphur. The prismatic crystals are brown, transparent, and less dense than the crystals of rhombic sulphur, their specific gravity being only 1·93, and their melting point is higher—about 120°. These crystals of sulphur cannot be kept at the ordinary temperature, which is already seen from the fact that in time they turn yellow ; also the specific gravity changes, and they pass completely into the ordinary modification. This is accompanied by a considerable development of heat, so that the temperature of the mass may rise 12°. Thus sulphur is *dimorphous*—that is, it exists in two crystalline forms, and in both forms it has independent physical properties. However, no chemical reactions are known which distinguish the two modifications of sulphur, just as there are none distinguishing aragonite from calcspar.[9]

If molten sulphur be heated to 150°, it loses its mobility, and becomes thick and very dark-coloured, so that the vessel containing it may be inverted without the sulphur running out. When heated above 300°, the sulphur again becomes liquid, although it does not acquire its original colour, and at 440° it boils. These modifications in the properties of sulphur depend not only on the variations of temperature, but also on a change of structure. If sulphur, heated to about 350°,

[8] If the experiment be made in a vessel with a narrow capillary tube, the sulphur fuses at a lower temperature (occurs, as it were, in a supersaturated state), and, solidifying at 90°, appears in a rhombic form (Schützenberger).

[9] If sulphur be cautiously melted in a U tube immersed in a salt bath, and then gradually cooled, it is possible for all the sulphur to remain liquid at 100°. It will now be in a state of superfusion; thus also by careful refrigeration water may be obtained in a liquid state at −10°, and a lump of ice then causes such water to separate out ice, and the temperature rises to 0°. If a prismatic crystal of sulphur be thrown into one branch of the U tube containing the liquid sulphur at 100°, and an octahedral crystal be thrown into the other branch, then, as Gernez showed, the sulphur in each branch will crystallise in corresponding forms, and both forms are obtained at the same temperature; therefore it is not the influence of temperature only which causes the molecules of sulphur to distribute themselves in one or another form, but also the influence of the crystalline parts already formed. This phenomenon is essentially analogous to the phenomena of supersaturated solutions.

be poured in a thin stream into cold water, it does not solidify into a solid mass, but retains its brown colour and *remains soft*, may be stretched out into threads, and is elastic, like guttapercha. But in this soft and ductile state, also, it does not remain for a long time. After the lapse of a certain period this soft transparent sulphur hardens, becomes opaque, passes into the ordinary yellow modification of sulphur, and, in so doing, develops heat, just as in the conversion of the prismatic into the octahedral variety. The soft sulphur is characterised by the fact that a certain portion of it is insoluble in carbon bisulphide. When soft sulphur is immersed in this liquid, then only a portion of common sulphur passes into solution, whilst a certain portion is quite insoluble, and remains so for a long time. The maximum proportion of insoluble sulphur is obtained by heating slightly above 170°. It melts at 114°. An exactly similar *insoluble amorphous sulphur* is obtained in certain reactions in the wet way, when sulphur separates out from solutions. Thus sodium thiosulphate, $Na_2S_2O_3$, when treated with acids, gives a precipitate of sulphur, which is insoluble in carbon bisulphide. The action of water on sulphur chloride also gives a similar modification of sulphur. Certain sulphides, when treated with nitric acid, also yield sulphur in this form.[10]

[10] A certain amount of insoluble sulphur remains for a long time in the mass of soft sulphur, changing into the ordinary variety. Freshly-cooled soft sulphur contains about one-third of insoluble sulphur, and after the lapse of two years it still contains about 15 p.c. Flowers of sulphur, obtained by the rapid condensation of sulphur from a state of vapour, also contains a certain amount of insoluble sulphur. *Rapidly distilled and condensed sulphur* also contains some insoluble sulphur. Hence a certain amount of insoluble sulphur is frequently found in roll sulphur. The action of light on a solution of sulphur converts a certain portion into the insoluble modification. Insoluble sulphur is of a lighter colour than the ordinary variety. It is best prepared by vaporising sulphur in a stream of carbonic anhydride, hydrochloric acid, &c., and collecting the vapour in cold water. When condensed in this manner it is nearly all insoluble in carbon bisulphide. It then has the form of hollow spheroids, and is therefore lighter than the common variety: sp. gr. 1·82. An idea of the modifications taking place in sulphur between 110° and 250° may be formed from the fact that at 150° liquid sulphur has a coefficient of expansion of about 0·0005, whilst between 150° and 250° it is less than 0·0003.

When a solution of sulphuretted hydrogen in water is decomposed by an electric current the sulphur is deposited on the positive pole, and has therefore an electro-negative character, and this sulphur is soluble in carbon bisulphide. When a solution of sulphurous acid is decomposed in the same manner, the sulphur is deposited on the negative pole, and is therefore electro-positive, and the sulphur so deposited is insoluble in carbon bisulphide. The sulphur which is combined with metals must have the properties of the sulphur contained in sulphuretted hydrogen, whilst the sulphur combined with chlorine is like that which is combined with oxygen in sulphurous anhydride. Hence Berthelot recognises the presence of soluble sulphur in metallic sulphides, and of the insoluble modification of amorphous sulphur in sulphur chloride. Cloez showed that the sulphur precipitated from solutions is either soluble or insoluble, according as to whether it separates from an alkaline or acid solution. If sulphur be melted with

At temperatures of 440° to 700° the vapour density of sulphur is 6·6 referred to air—*i.e.*, about 96 referred to hydrogen. Hence, at these temperatures *the molecule of sulphur contains six atoms*; it has the composition S_6. The agreement between the observations of Dumas, Mitscherlich, Bineau, and Deville confirms the accuracy of this result. When heated to temperatures above this—namely, *at a temperature above* 800° to 1000°—sulphur rapidly changes its vapour density with respect to that of hydrogen or air. At these temperatures the vapour density of sulphur referred to air is 2·2, which is equal to about 32 referred to hydrogen. At this temperature *the molecule of sulphur*, like that of hydrogen, oxygen, nitrogen, and chlorine, contains *two atoms*; hence the molecular formula is then S_2. This variation in the vapour density of sulphur evidently corresponds with a polymeric modification of sulphur, and may be likened to the transformation of ozone, O_3, into oxygen, O_2, or, better still, of benzene, C_6H_6, into acetylene, C_2H_2.[11]

a small quantity of iodine or bromine, then on pouring out the molten mass it forms amorphous sulphur, which keeps for a very long time, and is insoluble, or nearly so, in carbon bisulphide. This is taken advantage of for casting certain articles in sulphur, which retain their tenacity for a long time; for example, the discs of electrical machines.

[11] Here, however, it is very important to remark that both benzene and acetylene can exist at the ordinary temperature, whilst the sulphur molecule S_2 only exists at high temperatures; and if this sulphur be allowed to cool, it first passes into S_6 and then into a liquid state. Were it possible to have sulphur at the ordinary temperature in both the above modifications, then in all probability the sulphur in the state S_2 would present totally different properties from those which it has in the form S_6, just as the properties of gaseous acetylene are far from being similar to those of liquid benzene, which boils at 80°. Sulphur, in the form S_2, is probably a substance which boils at a much lower temperature than the variety with which we are now dealing. Paterno and Nasini (1888), following Raoult's method (that is, the fall of freezing-point in a benzene solution), found that the molecule of sulphur in solution contains S_6. But the problem of this aspect of the matter cannot as yet be considered as ultimately solved.

One cannot but here turn attention to the fact that sulphur, with all its analogy to oxygen (which also shows itself in its faculty to give the modification S_2), is also able to give a series of compounds containing more sulphur than the analogous compounds of oxygen. So, for instance, compounds of 5 atoms of sulphur with 2 atoms of potassium, or with 1 atom of barium, are known. In every case one cannot but see in sulphur a faculty for the union of a greater number of atoms than with oxygen. With oxygen the form of ozone, O_3, is very unstable, the stable form is O_2; whilst with sulphur S_6 is the stable form, and S_2 is exceedingly unstable. Furthermore, it is remarkable that sulphur gives a higher degree of oxidation H_2SO_4, corresponding, as it were, with its complex composition, if we suppose that in S_6 four atoms of sulphur are replaced by oxygen and one by two atoms of hydrogen. The formulæ of its compounds, K_2SO_4, $K_2S_2O_5$, K_2S_5, BaS_5, and many others, have no analogues among the compounds of oxygen. They all correspond with the form S_6 (one portion of the sulphur being replaced by oxygen and another by metals), which is not repeated by oxygen. In this faculty of sulphur to hold many atoms of other substances the same forces appear which cause many atoms of sulphur to form one complex molecule. This is also seen in other examples: oxygen gives H_2O and H_2O_2, and in an uncombined state O_2 and O_3; chlorine gives only HCl, and in a free state Cl_2; sulphur gives both H_2S and H_2S_2, and also H_2S_5, because

In its faculty for combination sulphur most closely resembles oxygen and chlorine ; like them, it combines with nearly all elements, with the development of heat and light, forming sulphur compounds which, as was said above, resemble the analogous oxygen compounds. Like oxygen, sulphur only combines with the majority of elements at a high temperature. At the ordinary temperature it does not enter into reactions, owing, amongst other things, to the fact that it is a solid. In a molten state it acts on the majority of substances—on the metals and the halogens. It combines with oxygen at about 400°, and with carbon at a red heat ; but it does not combine with nitrogen. The products of these reactions will be afterwards described, and we will now turn to the compounds of sulphur with hydrogen and the metals.

The majority of metals, when fused or heated with sulphur, combine with it. Fine wires, or the powders of the greater number of metals, burn in the vapour of sulphur. The direct combination of hydrogen with sulphur is restricted by a limit—that is, at a given temperature and other conditions it does not proceed unrestrictedly ; there is no explosion or recalescence. Sulphuretted hydrogen, H_2S, decomposes at its temperature of combination—that is, it is easily dissociated.[12] The same thing is repeated here as with water, only the limits of the temperatures at which the attraction of hydrogen for sulphur begins and ceases are much closer than in the case of oxygen and hydrogen. The temperature at which combination takes place is here, as in many other instances, the same as that at which dissociation begins. Therefore, *sulphuretted hydrogen* is formed in a small quantity

in a free state it is able to contain S_2 and S_6, and probably also S_4. If, as we know, there is an atomic analogy between ozone, O_3, and H_2O_2, so in H_2S_5 there would be an atomic analogy to S_6.

[12] In the formation of potassium sulphide, K_2S (that is, in the combination of 32 parts of sulphur with 78 parts of potassium), about 100 thousand heat units are developed. Nearly as much heat is developed in the combination of an equivalent quantity of sodium; about 90 thousand heat units in the formation of calcium or strontium sulphide, about 40 thousand for zinc or cadmium sulphide, and about 20 thousand for iron, cobalt, or nickel sulphide. Less heat is evolved in the combination of sulphur with copper, lead, and silver. According to Thomsen, sulphur develops heat with hydrogen in solutions; thus the reaction $I_2,Aq,H_2S = 21830$ calories—that is (in the presence of excess of water), a sufficient amount of heat is developed to raise the temperature of 21830 grams of water 1° C. But, as the reaction $I_2 + H_2 + Aq$ develops 26342 calories, it follows that the reaction $H_2 + S$ develops 4512 calories. We here add the amounts of heat developed by the combination of the other non-metals with hydrogen, also according to Thomsen, $(H,Cl) = 22001$; $(H,Br) = 8440$; $(H,I) = -6036$ (heat is absorbed); $(N,H_3) = 26707$; $(C,H_4) = 20420$; $(C_2,H_4) = 10880$; $(C_2,H_2) = -55010$. For the present it can only be said, with respect to combination with hydrogen, that in each group of non-metals the elements with small atomic weights (carbon, nitrogen, oxygen, chlorine) develop heat in combining with hydrogen, and those having larger atomic weights either develop less heat or absorb it (arsenic ?, selenium, tellurium ?, iodine).

by the direct ignition of a mixture of the vapour of sulphur and hydrogen. However, the temperature must not be high, because otherwise the whole of the sulphuretted hydrogen is decomposed; but at lower temperatures a small amount of sulphuretted hydrogen is formed by direct combination.[13] Sulphuretted hydrogen, like all other hydrogen compounds, may be easily obtained by the double decomposition of its corresponding metallic compounds, by replacing the metal by hydrogen by the action of acids on their sulphides. The metallic sulphides are, as a rule, easily formed, and some are even met with in nature. A sulphide, when mixed with a non-volatile acid, may give, by double decomposition, a salt of the acid taken and sulphuretted hydrogen, $M_2S + H_2SO_4 = H_2S + M_2SO_4$. However, it is not all sulphides nor solutions of all acids that will evolve sulphuretted hydrogen, which is exceedingly characteristic, because, for example, all carbonates evolve carbonic anhydride when treated with any acid. Sulphuric acid will only evolve sulphuretted hydrogen from those sulphides which contain a metal capable of decomposing the acid with the evolution of hydrogen. Thus zinc, iron, calcium, magnesium, manganese, potassium, sodium, &c., form sulphides which evolve sulphuretted hydrogen when treated with sulphuric acid, and the metals themselves evolve hydrogen with acids.[14] The sulphides of those metals which do not liberate

[13] If sulphur is melted in a flask and heated to nearly its boiling point, then, as Lidoff showed, the addition, drop by drop (from a funnel with a stop-cock) of heavy (0·9) naphtha oil (of lubricating oleonaphtha), &c., is followed by a regular evolution of sulphuretted hydrogen. This is analogous to the action of bromine or iodine on paraffin and other oils, because hydrobromic or hydriodic acid is then formed (Chapter XI.). A certain amount of hydrogen sulphide is even formed when sulphur is boiled with water.

[14] However, the matter is really much more complicated. Thus zinc sulphide evolves sulphuretted hydrogen with sulphuric or hydrochloric acids, but does not react with acetic acid and is oxidised by nitric acid. So, also, ferrous sulphide evolves sulphuretted hydrogen with acids, whilst the bisulphide, FeS_2, on the contrary, does not react with feeble acids. This absence of action depends, among other things, on the form in which the native iron pyrites occurs; it is a crystalline, compact, and very dense substance, which is totally insoluble in water; and acids in general react with great difficulty on such metallic sulphides. This is seen very clearly in the case of zinc sulphide; if this substance is obtained by double decomposition, it separates as a white precipitate which evolves sulphuretted hydrogen with great ease when treated with acids. Zinc sulphide is obtained in the same form when zinc is fused with sulphur, but native zinc sulphide—which occurs in compact masses, known under the name of zinc blende, and has a metallic lustre—is not decomposed or scarcely decomposed by sulphuric acid.

Another source of complication in the behaviour of the metallic sulphides towards acids depends on the action of water, and is shown in the fact that the action varies with different degrees of dilution or proportion of water present. The best known example of this is seen with antimonious sulphide, Sb_2S_3, because strong hydrochloric acid, containing not more water than corresponds with $HCl,6H_2O$, even decomposes native antimony glance, with evolution of sulphuretted hydrogen, whilst dilute acid has no action, and in the presence of an excess of water the reaction $2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl$ occurs, whilst in the presence of a small amount of water the reaction proceeds in

hydrogen from acids do not generally act on acids—that is, do not form sulphuretted hydrogen with them; such are, for example, the sulphides of lead, silver, copper, mercury, tin, &c. Therefore, the *modus operandi* of the formation of sulphuretted hydrogen by the action of acids on metallic sulphides may be looked on as a phenomenon of the combination of hydrogen, at the moment of its evolution, with the sulphur, which is combined with the metal. Such a representation is all the more simple, as all the circumstances under which sulphuretted hydrogen is formed are exactly similar to the conditions of the formation of hydrogen itself. Thus the usual mode of preparing sulphuretted hydrogen is by the action of *sulphuric acid on ferrous sulphide*, in which the same apparatus and method is employed as in the preparation of hydrogen, only replacing the metallic iron or zinc by ferrous sulphide or zinc sulphide. The reaction between sulphide of iron and sulphuric acid takes place at the ordinary temperature, and is accompanied by the same inconsiderable development of heat as in the liberation of hydrogen itself, $FeS + H_2SO_4 = FeSO_4 + H_2S$.[15]

In nature sulphuretted hydrogen is formed by many means. The most usual method of its formation is by the decomposition of albuminous substances containing sulphur, as has been mentioned above. Another method by which sulphuretted hydrogen is formed in nature is by the reducing action of organic matter on sulphates, and by the

exactly the opposite direction. Here the participation of water in the reaction and its affinity are evident, and this is clearly expressed in the thermochemical data, as has been partially explained previously, especially in Chap. X, Note 27.

The facts that lead sulphide is insoluble in acids, that zinc sulphide is soluble in hydrochloric acid but insoluble in acetic acid, that calcium sulphide is even decomposed by carbonic acid, &c.—all these peculiarities of the sulphides are in correlation with the amount of heat evolved in the reaction of the oxides with hydrogen sulphide and with acids, as is seen from the observations of Favre and Silberman, and from the comparisons made by Berthelot in the Proceedings of the Paris Academy of Sciences, 1870, to which we refer the reader for further details.

[15] *Ferrous sulphide* is formed by heating a piece of iron to an incipient white heat, and then removing it from the furnace and bringing it into contact with a piece of sulphur. Combination then proceeds, accompanied by the development of heat, and the ferrous sulphide formed fuses (Vol. I. p. 8). The sulphide of iron thus formed is a black, easily-fusible substance, insoluble in water. When damp it attracts oxygen from the air, and is converted into green vitriol, $FeSO_4$. If all the iron does not combine with the sulphur in the method described above, the action of sulphuric acid will evolve hydrogen as well as hydrogen sulphide.

We will not describe the details respecting the preparation of sulphuretted hydrogen employed as a reagent in the laboratory, because, in the first place, the methods are essentially the same as in the preparation of hydrogen, and, in the second place, because the apparatus and method employed are always described in text-books of analytical chemistry. Ferrous sulphide may be advantageously replaced by calcium sulphide or a mixture of calcium and magnesium sulphides. A solution of magnesium hydrosulphide, MgS,H_2S, is very convenient, as at 60° it evolves a stream of pure hydrogen sulphide.

action of water and carbonic acid on the sulphides formed by this reduction. A third source of sulphuretted hydrogen in nature is by volcanic eruptions. Although sulphuretted hydrogen is formed in small quantities everywhere in nature, it nevertheless soon disappears from the atmosphere, owing to its being easily decomposed by oxidising agencies. Many mineral waters contain sulphuretted hydrogen, and smell of it; they are called 'sulphur waters.'

Sulphuretted hydrogen, at the ordinary temperature, is a colourless gas, having a very unpleasant odour. It has, as its composition H_2S shows, a specific gravity seventeen times greater than hydrogen, and therefore it is somewhat heavier than air. Sulphuretted hydrogen *liquefies* at about $-74°$, and at the ordinary temperature when subjected to a pressure of 10 to 15 atmospheres; at $-85°$ it is converted into a solid crystalline mass. Liquid sulphuretted hydrogen is most easily obtained by the decomposition of hydrogen polysulphide, which we shall presently describe, by the action of heat, and in the presence of a small amount of water. If poured into a bent tube, like that described for the liquefaction of ammonia (Vol. I. p. 248), the hydrogen polysulphide is decomposed by heat, in the presence of water, into sulphur and sulphuretted hydrogen, which condenses in the cold end of the tube into a colourless liquid. The easy liquefaction of sulphuretted hydrogen is evidently allied to its solubility. One volume of water at 0° dissolves 4·37 volumes of sulphuretted hydrogen, at 10° 3·58 volumes, and at 20° 2·9 volumes.[16] The solutions impart a very feeble red coloration to litmus paper. This gas not only has a very unpleasant odour, but it is poisonous. One part in fifteen hundred parts of air will kill birds. Mammalia die in an atmosphere containing $\frac{1}{200}$ of this gas.

Sulphuretted hydrogen is very easily *decomposed* into its component parts by the action of heat or a series of electric sparks. Hence it is not surprising that sulphuretted hydrogen undergoes change under the action of many substances having a considerable affinity for hydrogen and oxygen. Very many metals[17] evolve hydrogen with sulphuretted

[16] Sulphuretted hydrogen is still more soluble in alcohol than in water; one volume at the ordinary temperature dissolves as much as eight volumes of the gas. The solutions in water and alcohol undergo change, especially in open vessels, owing to the fact that the water and alcohol dissolve oxygen from the atmosphere, and this acts on the sulphuretted hydrogen, forming water and sulphur. The solution may be so altered in this manner that every trace of sulphuretted hydrogen disappears. Solutions of sulphuretted hydrogen in glycerin change much more slowly, and may therefore be kept for a long time as reagents. De Forcrand obtained a hydrate, $H_2S,16H_2O$, resembling the hydrates given by many gases. The data given by Cailletet and De Forcrand show that at 30° this crystallo-hydrate breaks up, even under pressure.

[17] Some metals evolve hydrogen from sulphuretted hydrogen at the ordinary tem-

hydrogen, so that in this respect it presents the property of an acid; for instance, $2H_2S+Sn=2H_2+SnS_2$. This may be taken advantage of for determining the composition of sulphuretted hydrogen, because a given volume then leaves the same volume of hydrogen. On the other hand, oxygen,[18] chlorine,[19] and even iodine decompose sulphuretted hydrogen, removing the hydrogen from it and leaving free sulphur, so that in this reaction the sulphur is replaced by the above-named elements; for example, $H_2S+Br_2=2HBr+S$. In no other hydrogen compound is it so easy to show the *substitution*, both of hydrogen and of the element combined with it, as in hydrogen sulphide. This clearly shows the feeble union between the elements forming this gas. Compounds containing a considerable amount of oxygen, and which easily part with it, can accomplish the separation of the sulphur very easily. Such are, for instance, nitrous acid, chromic acid, and even ferric oxide and the higher oxides like it. Thus, if sulphuretted hydrogen be passed into a solution of chromic acid or an acid solution of ferric oxide, then the oxygen of the substance in solution acts on the hydrogen of the sulphuretted hydrogen and forms water, *and the sulphur is separated in a free state.* Thus, sulphuretted hydrogen acts as a *reducing agent*, in virtue of the hydrogen it contains. Salts of iodic, chlorous, chloric, and other acids are reduced by sulphuretted hydrogen, their oxygen acting mainly on the hydrogen of the sulphuretted hydrogen; but, in the presence of an excess of a powerful oxidising agent a portion of the sulphur may also be oxidised into sulphurous anhydride. The reducing action of sulphuretted hydrogen is frequently applied in chemical manipulations for the preparation of lower oxides, and for the conversion of certain oxygen compounds into hydrogen compounds; thus, the higher oxides of nitrogen are converted into ammonia by it, and in the presence of alkalis the nitro-compounds are converted into ammonia derivatives. The reaction of sulphuretted

perature. For example, the light metals, and copper and silver (especially with the access of air?) among the heavy metals. Hence articles made of silver turn black in the presence of vapours containing sulphuretted hydrogen, because silver sulphide is black. Mercury also decomposes sulphuretted hydrogen at the ordinary temperature, but slowly, like the above two metals, and therefore although sulphuretted hydrogen may be collected over mercury, it cannot be kept along with it. Zinc and cadmium act at a red heat, but not completely.

[18] If sulphuretted hydrogen escapes from a fine orifice into the air, it will burn when lighted, and be transformed into sulphurous anhydride and water. But if it burns in a limited supply of air—for instance, when a cylinder is filled with it and lighted—then only the hydrogen burns, which has, judging from the amount of heat developed in its combustion and from all its properties, a greater affinity for oxygen than sulphur. In this respect the combustion of sulphuretted hydrogen resembles that of hydrocarbons.

[19] Hence bleaching powder and chlorine destroy the stench of sulphuretted hydrogen. (For the reaction of hydrogen sulphide and iodine, *see* Vol. I. p. 498.)

hydrogen on sulphurous anhydride belongs to this class of phenomena, the chief products of which are sulphur and water, $2H_2S+SO_2=2H_2O+S_3$.

The acid character of sulphuretted hydrogen is clearly seen in its action on alkalis and salts. Thus free lead oxide and its salts in the presence of sulphuretted hydrogen form water or an acid (if a salt were taken), and sulphide of lead: $PbX_2+H_2S=PbS+2HX$. This reaction even proceeds in the presence of powerful acids, because lead sulphide is one of those sulphides which are unacted on by acids, and the reaction proceeds to the end in solutions. This reaction is taken advantage of for the preparation of many acids, by first converting them into a lead salt, and then submitting this salt to the action of sulphuretted hydrogen. For example, lead formate with sulphuretted hydrogen gives formic acid and lead sulphide: $C_2H_2PbO_4+H_2S=PbS+2CH_2O_2$. But sulphuretted hydrogen acts in a similar manner also on a number of metallic acid substances in solution or in an anhydrous state: (1) if it does not reduce the acid; (2) if the sulphur compound corresponding with the anhydride of the acid be insoluble in water, the reaction proceeds in solutions; (3) if the sulphuretted hydrogen and the acid taken do not come in contact with an alkali, on which they would be able to act first; and (4) if the sulphur compound be not decomposed by water. Thus solutions of arsenious acid give a precipitate of arsenious sulphide, As_2S_3, with sulphuretted hydrogen. This reaction proceeds not only in the presence of water, but also of acids, because the latter do not decompose the resultant sulphur compounds. The type of the decomposition is the same as with bases—that is, the sulphur and oxygen change places: $RO_n+nH_2S=RS_n+nH_2O$. Some sulphides corresponding with acid anhydrides are decomposed by water, and therefore are not formed in the presence of water. Such, for example, are the sulphides of phosphorus.[20]

[20] The sulphide P_4S is obtained by cautiously fusing the requisite proportions of common phosphorus and sulphur under water; it is a liquid which solidifies at 0°, and may be distilled without undergoing change, but it fumes in air and easily takes fire. The higher sulphide, P_2S, has similar properties. But little heat is evolved in the formation of these compounds, and it may be thought that they are formed by the direct conjunction of whole molecules of phosphorus and sulphur; but if the proportion of sulphur be increased, the reaction is accompanied by so considerable a rise of temperature that an explosion takes place, and for the sake of safety red phosphorus must be used and mixed as intimately as possible with powdered sulphur and heated in an atmosphere of carbonic anhydride. The higher compounds are decomposed by water. By increasing the proportion of sulphur, the following compounds have been obtained: P_4S_3 as prisms (fuses at 165°, Rebs), soluble in carbon bisulphide, and unaltered by air and water; *phosphorus trisulphide*, P_2S_5, is the analogue of P_2O_5; it is a light yellow crystalline compound only slightly soluble in carbon bisulphide, fusible and volatile and decomposed into hydrogen sulphide and phosphorous acid by water, and, like the highest compound of

The metallic sulphides corresponding with the metallic oxides have either a feeble alkaline or a feeble acid character, according to the character of the corresponding oxide, and therefore by combining together they are able to form saline substances—that is, salts in which the oxygen is replaced by sulphur. Thus sulphuretted hydrogen having the properties of a feeble acid[21] has, at the same time, the properties of water, and forms the type of the sulphur derivatives, which may also be formed by means of sulphuretted hydrogen, just as the oxides may be formed by the aid of water. But as sulphuretted hydrogen has acid properties, it combines more easily with the basic

sulphur and phosphorus, P_2S_5, it forms thio- salts with potassium sulphide, &c. This *phosphorus pentasulphide* corresponds with phosphoric anhydride; like the trisulphide, it gives hydrogen sulphide and phosphoric acid with an excess of water. It reacts in many respects like phosphoric chloride. The sulphide PS_2 is also known; the vapour density of this compound seems to indicate a molecule P_3S_6.

Phosphorus sulphochloride, $PSCl_3$, corresponds with phosphorus oxychloride. It is a colourless, pleasant-smelling liquid, boiling at 124°, and of sp. gr. 1·63; it fumes in air and is decomposed by water: $PSCl_3 + 4H_2O = PH_3O_4 + H_2S + 3HCl$. It is obtained when phosphoric chloride is treated with hydrogen sulphide, hydrochloric acid being also formed; it is also formed by the action of phosphoric chloride on certain sulphides—for example, on antimonious sulphide, also by the (cautious) action of phosphorus on sulphur chloride: $2P + 3S_2Cl_2 = 2PSCl_3 + 4S$, and even in the reaction $3PCl_5 + SOCl_2 = PCl_5 + POCl_3 + PSCl_3$, showing the reducing action of phosphorus trichloride, which is especially clear in the reaction $SO_3 + PCl_3 = SO_2 + POCl_3$. Thorpe and Rodger (1889), by heating lead fluoride with phosphorus pentasulphide, obtained thiophosphoryl fluoride as a colourless, spontaneously-inflammable gas.

[21] In characterising the acid properties of sulphuretted hydrogen it is very important, however, to remark that sulphuretted hydrogen, like water, does not saturate the alkaline properties of alkali hydroxides, so that a solution of potassium hydroxide will not under any circumstances give a neutral liquid with sulphuretted hydrogen. In this case the sulphuretted hydrogen forms in solution only an acid salt with the potassium: $KHO + H_2S = KHS + H_2O$. One must suppose that the normal salt is not formed in the solution—that is, that the reaction $2KHO + H_2S = K_2S + 2H_2O$ does not take place. This is seen from the fact that a development of heat, depending on the formation of potassium hydrosulphide, KHS, is remarked when as much hydrogen sulphide is passed into a solution of potassium hydroxide as it will absorb. But if a further quantity of potassium hydroxide be added to the resultant solution, heat is not developed, whilst if alkali be added to potassium acid sulphate or sodium acid carbonate heat is developed. From this it must not be concluded (as Thomsen concludes) that hydrogen sulphide is a monobasic acid. The impropriety of this conclusion is not only seen from the decomposing action of water on potassium sulphide, but also from the fact that for the formation of this salt there must react ($KHS + KHO = K_2S + H_2O$) substances which closely resemble each other, and in such cases hardly any heat is developed—for example, in double decompositions between salts. The resultant substances, potassium sulphide and water, undoubtedly act on each other, and thus would cause the absorption of heat did not the reaction of potassium hydrosulphide with potassium hydroxide also develop heat. Furthermore, it must be taken into account that potassium oxide, K_2O, and the anhydrous oxides like it, also do not exist in solutions, and whenever they might be formed they immediately react with the water, forming caustic potash, KHO, &c. In this sense, directly potassium sulphide, K_2S, is formed in water it is decomposed into potassium hydroxide and hydrosulphide: $K_2S + H_2O = KHO + KHS$. Potassium sulphide, K_2S, in a solid state corresponds with K_2O, although neither can exist in solution.

metallic sulphides. Hence, for instance, there exists, a compound of sulphuretted hydrogen with potassium sulphide, potassium hydrosulphide, $2KHS = K_2S + H_2S$, just as there are potassium hydroxides; but there are scarcely any compounds of sulphuretted hydrogen with the sulphides corresponding with acids. Thus sulphuretted hydrogen corresponds with the sulphides of the metals, and these may be regarded either as salts of sulphuretted hydrogen or as oxides of the metals in which the oxygen is replaced by sulphur. In general terms the sulphides exhibit the same degrees of difference with respect to their solubility in water as do the oxides. Thus the oxides of the alkali metals, and of some of the metals of the alkaline earths, are soluble in water, whilst those of nearly all the other metals are insoluble. The same may be said as to the sulphides; the sulphides of the metals of the alkalis and of the alkaline earths are soluble in water, whilst those of the other metals are insoluble. Those metals, like aluminium, whose oxides—for example, Al_2O_3—have intermediate properties and do not form compounds with feeble acids, at least in a wet way, also do not form sulphides by this method, although these may be obtained indirectly. The sulphides of the other metals are even formed in a wet way, and with particular ease if they are insoluble in water. In this case their salts enter into double decomposition with sulphuretted hydrogen, or with soluble sulphides, and give an insoluble sulphide—for instance, a salt of lead gives lead sulphide with sulphuretted hydrogen. The sulphuretted hydrogen then separates the metal from its salts in a state of combination with sulphur, if the corresponding sulphide be insoluble in acid, as, for example, lead sulphide. This depends on the fact that by the action of sulphuretted hydrogen on a salt of such a metal, a free acid must be formed besides the metallic sulphide. Thus if a metal M be in a state of combination MX_2, then by the action of sulphuretted hydrogen there will be formed, besides MS,[22] an acid 2HX. It is evident that sulphuretted hydrogen will not precipitate an insoluble sulphide from the salts of those metals whose sulphides react with free acid, such as

[22] During the last seven years (Schulze, 1882) it has been found that many metallic sulphides which were considered totally insoluble do, under certain circumstances, form very unstable solutions in water, as has been mentioned in Vol. I. p. 96, Note 57. To what has already been mentioned in that note it is impossible to add anything more definite than that a colloidal state and a passage into solution are also known for many oxides (silica, alumina, stannic oxide, molybdic acid, and others), and the analogy of the phenomena of this class leads one to hope for the appearance of further generalisation and systematic research in this direction. Arsenic sulphide is very easily obtained in the form of a solution (hydrosol). Solutions of copper and cadmium sulphides may also be easily obtained by precipitating their salts CuX_2, or CdX_2, with ammonium sulphide, and washing the precipitate; but they are re-precipitated by the addition of foreign salts,

zinc, iron, manganese, &c., because free acid would be formed by the reaction of the sulphuretted hydrogen, and would be able to act on the sulphide formed. The reaction $FeCl_2 + H_2S = FeS + 2HCl$, and the like, do not take place, because the acid acts on the ferrous sulphide. Antimonious sulphide is not acted on by dilute hydrochloric acid, but it is decomposed by strong acid, and therefore in presence of an excess of hydrochloric acid antimonious chloride does not entirely react with hydrogen sulphide, whilst the reaction $2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl$ will go on to the end in a dilute solution and with a small quantity of acid. Those metallic sulphides which are decomposed by acids may be obtained in a wet way by the double decomposition of the salts of the metals, not with hydrogen sulphide, but with soluble metallic sulphides, such as sulphide of ammonium or of potassium, because then no free acid is formed, but a salt of the metal (potassium or ammonium) which was taken as a soluble sulphide. So, for example, $FeCl_2 + K_2S = FeS + 2KCl$.[23]

[23] In reality, the preceding reaction should be expressed thus: $FeCl_2 + 2KHS = FeS + 2KCl + H_2S$. But as the sulphuretted hydrogen takes no part in the reaction, it is usual to express the formation of such sulphides without taking the hydrogen sulphide proceeding from the potassium or ammonium hydrosulphides into account. It is not usual to employ potassium sulphide but ammonium sulphide—or, to speak more truly, ammonium hydrosulphide—in order to avoid the formation of a non-volatile salt of potassium in the solution, and to have, together with the formation of the sulphide, a salt of ammonium in solution, which can always be driven off by evaporating the solution and igniting the residue—for instance:

$$FeCl_2 + (NH_4)_2S = FeS + 2NH_4Cl, \quad \text{or} \quad FeCl_2 + 2(NH_4)HS = FeS + 2NH_4Cl + SH_2.$$

Thus the metallic sulphides may be divided into three chief classes: (1) *those soluble in water*, (2) *those insoluble in water but reacting with acids*, and (3) *those insoluble in both water and acids*. The third class may be easily subdivided into two groups; to the first group belong those sulphides which correspond with bases or basic oxides, and are therefore unable to play the part of an acid with the sulphides of the alkalis, and are insoluble in the alkali sulphides; whilst the sulphides of the second group are of an acid character, and give soluble salts with the sulphides of the alkaline metals, in which they play the part of an acid. To this group belong those metals whose corresponding oxides have very feeble basic properties or sharply-defined acid properties. It must be observed, however, that not all metallic acids have corresponding sulphides, partly owing to the fact that certain acids are reducible by sulphuretted hydrogen, especially when their lower degrees of oxidation are of a basic character. Such are, for instance, the acids of chromium, manganese, &c. Sulphuretted hydrogen converts them into lower oxides, having the properties of bases. Those bases which do not combine with feeble acids, such as carbonic acid and hydrogen sulphide, give a precipitate of hydroxide with ammonium sulphide—for example, aluminium salts react in this manner. Thus aluminium sulphide, Al_2S_3, is decomposed by water, and magnesium sulphide, MgS, gives magnesium hydrosulphide, $Mg(SH)_2$, and hydroxide, MgH_2O_2, with water. This difference of the metals in their behaviour towards sulphuretted hydrogen gives a very valuable means of separating them from each other, and *is taken advantage of in analytical chemistry*. If, for instance, the metals of the first and third groups occur together, it is enough to convert them into soluble salts, and to act on the solution of the salts with sulphuretted hydrogen; it will precipitate the

Metallic sulphides may be obtained by many other means besides the action of sulphuretted hydrogen on salts and oxides, or by the simple combination of metals with sulphur when heated or fused. Thus they may also be formed by the reduction of sulphates by heating them with charcoal or other means. Charcoal takes up the oxygen from many sulphates, leaving corresponding sulphides. Thus sodium sulphate, Na_2SO_4, when heated with charcoal, forms sodium sulphide, Na_2S, carbonic oxide and carbonic anhydride being evolved. Besides which metallic sulphides are also obtained by heating metals or their oxides in the vapours of many sulphur compounds—for example, in the vapour of carbon bisulphide, when the carbon takes up the oxygen of the oxide and the sulphur combines with the metal. The sulphides formed in this manner are often crystalline—that is, appear with those properties and in that crystalline form in which they occur in nature. Besides which we must mention the following general reactions common to all the sulphides of the metals. They are oxidised in air at the

metals of the third group in the form of sulphides, whilst the metals of the first group will not be in the least acted on. Such a method of separating the metals is more fully considered in analytical chemistry, and therefore we will here limit ourselves to pointing out to which groups the most common metals belong, and the colour which is proper to the sulphide precipitated.

Metals which are precipitated by sulphuretted hydrogen, as sulphides from a solution of their salts, even in the presence of free acid:

The precipitate is soluble in ammonium sulphide:

Platinum (dark brown)	*Antimony* (orange)
Gold (dark brown)	*Arsenic* (yellow).
Tin (yellow and brown)	

The precipitate is insoluble in ammonium sulphide:

Copper (black)	*Mercury* (black)
Silver (black)	*Lead* (black).
Cadmium (yellow)	

Metals which are precipitated by ammonium sulphide from neutral solutions, but not precipitated from acid solutions by sulphuretted hydrogen:

The sulphide precipitated is soluble in hydrochloric acid:

Zinc (white) | *Manganese* (rose colour) | *Iron* (black)

The sulphide precipitated is not soluble in dilute hydrochloric acid:

Nickel (black) | *Cobalt* (black)

A hydroxide, and not a sulphide, is precipitated:

Chromium (green) | *Aluminium* (white).

The metals of the alkalis and of the alkaline earths are not precipitated by either sulphuretted hydrogen or ammonium sulphide. The metals of the alkaline earths when in acid solutions in the form of phosphates and many other salts are precipitated by ammonium sulphide, because it neutralises the free acid, with formation of an ammonium salt of the acid and evolution of sulphuretted hydrogen.

ordinary, and especially at a higher, temperature, forming sulphates in the majority of cases. This oxidation proceeds with particular ease, even at the ordinary temperature, when a metallic sulphide is precipitated from its solutions, as a fine powder containing water. The sulphides of iron and manganese, &c., are very easily oxidised in this manner. But if these hydrates be ignited, they lose their water (the ignition must be carried on in a stream of hydrogen to prevent their oxidation during the process), and then they are no longer oxidised at the ordinary temperature. Those sulphides whose corresponding sulphates are decomposed by heat part with their sulphur in the form of sulphurous anhydride, when they are ignited in air, and the metal, as a rule, remains behind as oxide. This is taken advantage of in the treatment of sulphurous ores. The process is called *roasting*.

Hydrogen not only forms sulphuretted hydrogen with sulphur, but it also combines with it in several other proportions, just as it combines with oxygen, forming not only water, but also hydrogen peroxide. And these *polysulphides of hydrogen* are also unstable, like hydrogen peroxide, and are also obtained from the corresponding polysulphides of the metals of the alkaline earths, just as hydrogen peroxide is obtained from barium peroxide—that is, from a polyoxygen compound. Thus calcium combines with sulphur in several proportions, forming not only calcium sulphide, CaS, but also as bi-, tri-, and pentasulphide, CaS_5, and all these compounds are soluble in water. Sodium also combines with sulphur in the same proportions, forming sulphides from Na_2S to Na_2S_5. If an acid is added to a solution of a polysulphide, it gives sulphur, sulphuretted hydrogen, and a salt of the metal. For instance, with a pentasulphide: $MS_5 + 2HCl = MCl_2 + H_2S + 4S$. If we reverse the operation, and pour a solution of a polysulphide into an acid, then sulphur is not precipitated, but an oily liquid is formed, which is heavier than water and insoluble in it. This oily substance is the polysulphide of hydrogen: $MS_5 + 2HCl = MCl_2 + H_2S_5$. As Rebs showed (1888), whatever polysulphide be taken—of sodium, for instance—it always gives one and the same *hydrogen pentasulphide*,[24] of specific gravity 1·71 (15°). It can only be preserved in the absence of water and at low temperatures, and then not for long; for, especially

[24] Rebs took di-, tri-, tetra-, and penta-sulphides of sodium, potassium, and barium, which he prepared by dissolving sulphur in solutions of the normal sulphides; on adding hydrochloric acid he always obtained hydrogen pentasulphide, whence it is evident that $4H_2S_n = (n-1)H_2S_5 + (5-n)H_2S$. For example, if H_2S_2 were formed, it would decompose according to the equation $4H_2S_2 = H_2S_5 + 3H_2S$. The hydrogen pentasulphide formed breaks up into hydrogen sulphide and sulphur when brought into contact with water. Previous to Rebs' researches many chemists stated that all polysulphides gave the bisulphide H_2S_2, and Hofman recognised only hydrogen tri-sulphide, H_2S_3.

in the presence of alkalis and when slightly warmed, it splits up very easily into sulphuretted hydrogen and sulphur.[25]

The soluble sulphides and polysulphides of the metals of the alkalis and alkaline earths—for example, of ammonium,[26] potassium,[27] and

[25] The formation of the polysulphides of hydrogen, H_2S_n, is easily understood from the law of substitution, like that of the saturated hydrocarbons, C_nH_{2n+2}, knowing that sulphur gives H_2S and carbon CH_4, because the molecule of sulphuretted hydrogen may be divided into H and HS. This radicle, HS, is equivalent to H. But substituting this radicle for hydrogen in H_2S we obtain $(HS)HS = H_2S_2$, $(HS)(HS)S = H_2S_3$, &c., in general H_2S_n. The homologues of CH_4, C_nH_{2n+2} are thus formed from CH_4, and consequently the polysulphides H_2S_n are the homologues of H_2S. The question arises why in H_2S_n the the apparent limit of n is 5—that is, why does the substitution end with the formation of H_2S_5? The answer appears to me to be clearly because in the molecule of sulphur, S_6, there are six atoms of sulphur. The forces in one and the other case are the same. In the one case they hold S_6 together, in the other S_5 and H_2; and, judging from H_2S, the two atoms of hydrogen are equal in power and significance to the atom of sulphur. Just as hydrogen peroxide, H_2O_2, expresses the composition of ozone, O_3, in which O is replaced by H_2, so also H_2S_5 corresponds with S_6.

[26] *Ammonium sulphide*, $(NH_4)_2S$, may be prepared by passing sulphuretted hydrogen into a vessel full of dry ammonia, or if both dry gases be passed together into a very cold receiver. In the latter case it is necessary to prevent the access of air, and to have an excess of ammonia. Under these circumstances, two volumes of ammonia combine with one volume of sulphuretted hydrogen, and form a colourless, very volatile, crystalline substance having a very unpleasant odour, and which is very poisonous and exceedingly unstable. When exposed to the air it absorbs oxygen and acquires a yellow colour, and already contains oxygen and polysulphide compounds (because a portion of the hydrogen sulphide gives water and sulphur). It is soluble in water, and forms a colourless solution, which, however, in all probability contains free ammonia and the acid salt—that is, ammonium hydrosulphide, NH_4HS, or $(NH_4)_2S,H_2S$. This salt is formed when dry ammonia is mixed with an excess of dry sulphuretted hydrogen. When both gases come into contact at the ordinary or a higher temperature, they always combine in equal volumes: $(NH_4)HS = NH_3 + H_2S$. This compound crystallises in an anhydrous state in colourless plates, and may be easily volatilised (dissociating like ammonium chloride), even at the ordinary temperature; it has an alkaline reaction, absorbs oxygen from the air, is soluble in water, and its solution is usually prepared by saturating an aqueous solution of ammonia with sulphuretted hydrogen. According to the common rule, these salts, like other ammonium salts, split up into ammonia and sulphuretted hydrogen when they are distilled.

A solution of ammonium sulphide is able to dissolve sulphur, and it then contains compounds of hydrogen polysulphide and ammonia. Some of these compounds may be obtained in a crystalline form. Thus Fritzsche obtained a compound of ammonia with hydrogen pentasulphide, or ammonium pentasulphide, $(NH_4)_2S_5$, in the following manner: He saturated an aqueous solution of ammonia with sulphuretted hydrogen, added powdered sulphur to it, and then passed ammonia gas into the solution, which then absorbed a fresh amount. After this he again passed sulphuretted hydrogen into the solution, and then added sulphur, and then again ammonia. After repeating this several times, orange-yellow crystals separated out from the liquid. These crystals melted at 40° to 50°, and were very unstable.

When a solution of ammonium hydrosulphide, prepared by saturating a solution of ammonia with sulphuretted hydrogen, is exposed to the air it turns yellow, owing to the presence of an ammonium polysulphide, whose formation is due to the sulphuretted hydrogen being oxidised by the air and converted into water and sulphur, which is dis-

[27] See page 213.

calcium,[28]—have the appearance and properties of salts, just as the

solved by the ammonium sulphide. In certain analytical reactions it is usual to employ a solution of ammonium sulphide which has been kept for some time and acquired a yellow colour. This yellow sulphide of ammonium deposits sulphur when saturated with acids, whilst a freshly-prepared solution only evolves sulphuretted hydrogen. The yellow solution furthermore contains ammonium thiosulphate, which is derived not only from the oxidation of the ammonium sulphide, but also from the action of the liberated sulphur on the ammonia, just as an alkaline salt of thiosulphuric acid and a sulphide are formed by the action of sulphur on a solution of a caustic alkali.

[27] *Potassium sulphide*, K_2S, is obtained by heating a mixture of potassium sulphate and charcoal to a bright-red heat. It may be prepared in solution by taking a solution of potassium hydroxide, dividing it into two equal parts, and saturating one portion with sulphuretted hydrogen so long as it is absorbed. This portion will then contain the acid salt KHS. The two portions are then mixed together, and the potassium sulphide will then be obtained in the solution. This solution has a strongly alkaline reaction, and is colourless when freshly prepared, but it very easily undergoes change when exposed to the air, forming potassium thiosulphate and polysulphides. When the solution is evaporated at low temperatures under the receiver of an air-pump, it yields crystals containing $K_2S,5H_2O$. If left under the receiver of the air-pump, or heated at 150°, they part with 3 mol. H_2O, and at higher temperatures they lose nearly all their water without evolving sulphuretted hydrogen. When they are ignited in glass vessels they corrode the glass. When a solution of caustic potash, perfectly saturated with sulphuretted hydrogen, is evaporated under the receiver of an air-pump it forms colourless rhombohedra of *potassium hydrosulphide*, $2(KHS),H_2O$. These crystals are deliquescent in the air, but do not change in a vacuum when heated up to 170°, and at higher temperatures they lose water but do not evolve sulphuretted hydrogen. The anhydrous compound, KHS, fuses at a dark-red heat into a very mobile yellow liquid, which gradually becomes darker in colour and solidifies into a red mass. It is remarkable that when a solution of the compound KHS is boiled it somewhat easily evolves half of its sulphuretted hydrogen, leaving potassium sulphide, K_2S, in solution; and a solution of the latter in water is also able to evolve sulphuretted hydrogen under prolonged boiling, but the evolution cannot be rendered complete, and therefore, with a certain rise of temperature, a solution of potassium sulphide will not be capable of absorbing sulphuretted hydrogen at all. From this we must conclude that potassium hydroxide, water, and sulphuretted hydrogen form a system whose complex equilibrium is subject to the laws of dissociation, depends on the relative mass of each substance, on the temperature, and the dissociation pressure of the component elements. Potassium sulphide is not only soluble in water, but also in alcohol.

Berzelius showed that besides potassium sulphide there exists potassium bisulphide, K_2S_2; trisulphide, K_2S_3; tetrasulphide, K_2S_4; and pentasulphide, K_2S_5. According to the researches of Schöne, the three last are the most stable. These different compounds of potassium and sulphur may be prepared by fusing potassium hydroxide or carbonate with an excess of sulphur in a porcelain crucible in a stream of carbonic anhydride. At about 600° potassium pentasulphide is formed; this is the highest sulphur compound of potassium. When heated to 800° it loses one-fifth of its sulphur and gives the tetrasulphide, which at this temperature is as stable as the pentasulphide is at the lower temperature—that is, sulphur is not given off by it at this temperature. At a bright-red heat—namely, at about 900°—the trisulphide is formed. This compound may be also formed by igniting potassium carbonate in a stream of carbon bisulphide, in which case a compound, K_2CS_3, is first formed corresponding to potassium carbonate, and carbonic anhydride is evolved. On further ignition this compound splits up into carbon and potassium trisulphide, K_2S_3. The tetrasulphide may also be obtained in solution if a solution of potassium sulphide be boiled with the requisite amount of sulphur without

[28] See page 214.

hydrated oxides have the same appearance, whilst the sulphides of

the access of air. This solution yields red crystals of the composition $K_2S_4,2H_2O$ when it is evaporated in a vacuum. These crystals are very hygroscopic, easily soluble in water, but very sparingly in alcohol; when ignited they give off water, sulphuretted hydrogen, and sulphur. If a solution of potassium sulphide be boiled with an excess of sulphur it forms the pentasulphide, which, however, is decomposed by prolonged ebullition into sulphuretted hydrogen and potassium thiosulphate: $K_2S_5+3H_2O=K_2S_2O_3+3H_2S$. A substance called *liver of sulphur* was formerly frequently used in chemical practice and medicine. Under this name is known the substance which is formed by boiling a solution of caustic potash with an excess of flowers of sulphur. This solution contains a mixture of potassium pentasulphide and thiosulphate, $6KHO+12S=2K_2S_5+K_2S_2O_3+3H_2O$. The substance obtained by fusing potassium carbonate with an excess of sulphur was also known as liver of sulphur. If this mixture be heated to an incipient dark-red heat it will contain potassium thiosulphate, but at higher temperatures potassium sulphate is formed. In either case a polysulphide of potassium is also present.

[28] The metals of the alkaline earths, like those of the alkalis, form several compounds with sulphur; thus calcium forms compounds with one and with five atoms of sulphur. There are doubtless also intermediate sulphides, because the other metals of the alkaline earths form compounds with four and three atoms of sulphur. If sulphuretted hydrogen be passed over ignited lime it forms water and *calcium sulphide*, which may also be formed by heating calcium sulphate with charcoal, whilst if sulphur be heated with lime or with calcium carbonate, then naturally oxygen compounds (calcium thiosulphate and sulphate) are formed at the same time as calcium sulphide. The prolonged action of the vapour of carbon bisulphide, especially when mixed with carbonic anhydride, on strongly ignited calcium carbonate entirely converts it into sulphide. Calcium sulphide is generally obtained as a colourless, or slightly yellow, opaque, brittle mass, which is infusible at a white heat, and is soluble in water. When heated, dry calcium sulphide does not absorb oxygen from the air. An excess of water decomposes it, like many other metallic sulphides, precipitating lime and forming a hydrosulphide, CaH_2S_2, in solution. This compound is also formed by passing sulphuretted hydrogen through an aqueous solution of calcium sulphide or lime. Its solution, like that of calcium sulphide, has an alkaline reaction. It decomposes when evaporated, and absorbs oxygen from the air. *Calcium pentasulphide*, CaS_5, is not known in a pure state, but may be obtained in admixture with calcium thiosulphate by boiling a solution of lime or calcium sulphide with sulphur: $3CaH_2O_2+12S=2CaS_5+CaS_2O_3+3H_2O$. A similar compound in an impure form is formed by the action of air on alkali waste, and is used for the preparation of thiosulphates.

Many of the sulphides of the metals of the alkaline earths are phosphorescent—that is, they have the faculty of *emitting light in the dark*, after having been subjected to the action of sunlight, or of a bright source of light in general (Canton phosphorus, &c.). The luminosity lasts some time, but it is not durable, and gradually disappears. This faculty of being phosphorescent is proper, in a greater or less degree, to nearly all substances (Becquerel), but for a very short time, whilst with calcium sulphate it is comparatively durable, lasting for several hours. It is due to the excitation of the surfaces of substances by the action of light, and is determined by those rays which exhibit a chemical action. Hence daylight or the light of burning magnesium, &c., acts more powerfully than the light of a lamp, &c. Warnerke has recently shown that a small quantity of magnesium lighted near the surface of a phosphorescent substance rapidly excites the greatest possible intensity of luminosity; this enabled him to found a method of measuring the intensity of light—*i.e.*, to obtain a constant unit of light—and to apply it to photography. The nature of the change which is accomplished on the surface of the luminous substance is at present unknown, but in any case it is a renewable one, because the experiment may be repeated for an infinite number of times and takes place in a vacuum. The intensity and tint of the light emitted depend on the method of preparation of the calcium sulphide, and on the degree of ignition and purity of the calcium

the metals of the higher groups resemble their oxides and have not at all the appearance of salts, and this is especially true in the crystalline forms in which they frequently occur in nature.[29]

carbonate taken. According to the observations of Becquerel, the presence of compounds of manganese, bismuth, &c., sodium sulphide (but not potassium sulphide), &c., although in minute traces, is perfectly indispensable. This gives reason for thinking that the formation (in the dark) and decomposition (in light) of double salts like MnS,Na_2S perhaps forms the chemical cause of the phenomena. Compounds of strontium and barium have this property to even a greater extent than calcium sulphide. These compounds may be prepared as follows. For example, a mixture of sodium thiosulphate and strontium chloride is prepared; a double decomposition takes place between the salts, and, on the addition of alcohol, strontium thiosulphate, SrS_2O_3, is precipitated, which, when ignited, leaves strontium sulphide behind. The strontium sulphide thus prepared emits (when dry) a greenish yellow light. It contains a certain amount of sulphur, sodium sulphide, and strontium sulphate. By ignition at various temperatures, and by different methods of preparation, it is possible to obtain mixtures which emit different coloured lights.

[29] As examples, we will describe the sulphides of arsenic, antimony, and mercury. Arsenic trisulphide, or *orpiment*, As_2S_3, occurs native, and is formed in a pure form when a solution of arsenious anhydride in the presence of hydrochloric acid comes into contact with sulphuretted hydrogen (there is no precipitate in the absence of free acid). A beautiful yellow precipitate is then obtained: $As_2O_3 + 3H_2S = 3H_2O + As_2S_3$; it fuses when heated, and volatilises without decomposition. When fused it forms a semi-transparent, yellow mass, and it is thus that it enters the market. The specific gravity of native orpiment is 3·4, and that of the artificially-fused mass is 3·7. It is used as a yellow pigment, and owing to its insolubility in water and acids it is less injurious than the other compounds corresponding to arsenious acid. According to the type AsX_2, realgar, AsS, is known, but it is probable that the true composition of this compound is As_4S_4—that is, it presents the same relation to orpiment as liquid phosphuretted hydrogen does to gaseous. *Realgar* (*Sandaraca*) occurs native as brilliant red crystals of specific gravity 3·59, and may be prepared artificially by fusing arsenic and sulphur in the proportions indicated by its formulæ. It is prepared in large quantities by distilling a mixture of sulphur and arsenical pyrites. Like orpiment it dissolves in calcium sulphide, and even in caustic potash. It is used for signal lights and fireworks, because it deflagrates and gives a large and very brilliant white flame with nitre.

With antimony, sulphur gives a tri- and a penta-sulphide. The former, Sb_2S_3, which corresponds with antimonious oxide, occurs native (Chap. XIX.) in a crystalline form; its sp. gr. is then 4·9, and it presents brilliant rhombic crystals of a grey colour, which fuse when heated. A substance of the same composition is obtained as an amorphous orange powder by passing sulphuretted hydrogen into an acid solution of antimonious oxide. In this respect antimonious oxide again reacts like arsenious acid, and the sulphides of both are soluble in ammonium and potassium sulphides, and, especially in the case of arsenious sulphide, are easily obtained in colloidal solutions. By prolonged boiling with water, antimonious sulphide may be entirely converted into the oxide, hydrogen sulphide being evolved (Elbers). Native antimony sulphide, or the orange precipitated trisulphide when fused with dry, or boiled with dissolved, alkalis, forms a dark-coloured mass (Kermes mineral) formerly much used in medicine, and which contains a mixture of antimonious sulphide and oxide. There are also compounds of these substances. A so-called antimony vermilion is much used as a dye; it is prepared by boiling sodium thiosulphate (six parts) with antimony trichloride (five parts) and water (fifty parts). This substance probably contains an oxysulphide of antimony—that is, a portion of the oxygen in the oxide of antimony in it is replaced by sulphur. Red antimony ore, and antimony glass, which is obtained by fusing the trisulphide with antimonious oxide, has a similar composition, Sb_2OS_2. In practice, the *antimony penta-*

As the acids corresponding with chlorine, phosphorus, and carbon are the oxidised hydrogen compounds of these elements, so also we can form an idea of the acid hydrates of sulphur, or of *the normal acids of*

sulphide, Sb_2S_5, is the most frequently used of the sulphur compounds of antimony. It is formed by the action of acids on the so-called Schlippe's salt, which is a *sodium thiorthantimonate*, $SbS(NaS)_3$, corresponding with orthantimonic acid, $SbO(OH)_3$, with the replacement of oxygen by sulphur. It is obtained by boiling finely-powdered native antimony trisulphide with twice its weight of sodium carbonate, and half its weight of sulphur and lime, in the presence of a considerable quantity of water. The processes taking place are as follows:—The sodium carbonate is converted into hydroxide by the lime, and then forms sodium sulphide with the sulphur; the sodium sulphide then dissolves the antimony sulphide, which in this form already combines with the greatest amount of sulphur, so that a compound is formed corresponding with antimony pentasulphide dissolved in sodium sulphide. The solution is filtered and crystallised, care being taken to prevent access of air, which oxidises the sodium sulphide. This salt crystallises in large, yellowish crystals, which are easily soluble in water and have the composition $Na_3SbS_4,9H_2O$. When heated they lose their water of crystallisation and then fuse without alteration; but when in solution, and even in crystalline form, this salt turns brown in air, owing to the oxidation of the sulphur and the breaking up of the compound. As it is used in medicine, especially in the preparation of antimony pentasulphide, it is kept under a layer of alcohol, in which it is insoluble. Acids precipitate antimony pentasulphide from a solution of this salt, as an orange powder, insoluble in acids and very frequently used in medicine. This substance when heated evolves vapours of sulphur, and leaves antimony trisulphide behind.

Mercury forms compounds with sulphur of the same types as it does with oxygen. Mercurous sulphide, Hg_2S, easily splits up into mercury and mercuric sulphide. It is obtained by the action of potassium sulphide on mercurous chloride, and also by the action of sulphuretted hydrogen on solutions of salts of the type HgX. Mercuric sulphide, HgS, corresponding with the oxide, is *cinnabar;* it is obtained as a black precipitate by the action of an excess of sulphuretted hydrogen on solutions of mercuric salt. It is insoluble in acids, and is therefore precipitated in their presence. If a certain amount of water containing sulphuretted hydrogen be added to a solution of mercuric chloride, it first gives a white precipitate of the composition $Hg_3S_2Cl_2$—that is, a compound $HgCl,2HgS$, a sulphochloride of mercury like the oxychloride. But in the presence of an excess of sulphuretted hydrogen, the black precipitate of mercuric sulphide is formed. In this state it is not crystalline, but if it be heated to its temperature of volatilisation, it forms a red crystalline sublimate which is identical with native cinnabar. In this form its specific gravity is 8·0, and it forms a red powder, owing to which it is used as a red pigment (vermilion) in oil, pastel, and other paints. It is so little attacked by reagents that even nitric acid has no action on it, and the gastric juices do not dissolve it, so that it is not poisonous. When heated in air, the sulphur burns away and leaves metallic mercury. On a large scale cinnabar is usually prepared in the following manner: 800 parts of mercury and 115 parts of sulphur are mixed together as intimately as possible and poured into a solution of 75 parts of caustic potash in 425 parts of water, and the mixture is heated at 50° for several hours. Red mercury sulphide is thus formed, and separates out from the solution. The reaction which takes place is as follows: A soluble compound, K_2HgS_2, is first formed; this compound is able to separate in colourless silky needles, which are soluble in the caustic potash, but are decomposed by water, and at 50°; this solution (perhaps by attracting oxygen from the air) slowly deposits HgS in a crystalline form. A similar vermilion may be obtained by heating a mixture of mercury and sulphur; heat is evolved at the moment of combination, and a portion of the mass is volatilised.

I may here remark that lead sulphide in contact with zinc and hydrochloric acid gives sulphuretted hydrogen and metallic lead.

sulphur, by representing them as the oxidised products of sulphuretted hydrogen—

HCl	H_2S	H_3P	H_4C
$HClO$	$H_2SO(?)$	$H_3PO(?)$	H_4CO
$HClO_2$	$H_2SO_2(?)$	H_3PO_2	H_4CO_2
$HClO_3$	H_2SO_3	H_3PO_3	H_4CO_3
$HClO_4$	H_2SO_4	H_3PO_4	H_4CO_4 [30]

In the case of chlorine, if not all the hydrates, at all events salts of all the normal hydrates are known, whilst in the case of sulphur only the acids H_2S, H_2SO_3, and H_2SO_4 are known. But on the other hand, the latter are obtained not only as hydrates, but also as stable anhydrides, SO_2 and SO_3, which are formed with the evolution of heat from sulphur and oxygen; 32 parts of sulphur in combining with 32 parts of oxygen—that is, in forming SO_2—evolve 71000 heat units,[31] and if the oxidation proceeds to the formation of SO_3, 103000 heat units are evolved. These figures may be compared with those which correspond with the passage of carbon into CO and CO_2, when 29000 and 97000 units of heat are evolved. This determines the stability of the higher oxides of sulphur, and this expresses the peculiarity of sulphur as an element which, although an analogue of oxygen, forms stable compounds with it, and thus fundamentally differs from chlorine. The higher and lower oxides of chlorine are powerful oxidising agents, whilst the higher oxide of sulphur, SO_3, has but feeble oxidising powers, and the lower oxide, SO_2, frequently acts as a reducing agent, and is formed by the direct combustion of sulphur, just as carbonic anhydride, CO_2, proceeds from the combustion of carbon.

In the combustion of sulphur, and also in the oxidation of the sulphides and polysulphides by their ignition in air, *sulphurous oxide*, or *sulphurous anhydride*, or *sulphur dioxide*, SO_2, is exclusively formed. It is prepared on a large scale for the manufacture of sulphuric acid (Vol. I. p. 246), and for direct application in the manufacture of wine or for bleaching tissues and other purposes. In the latter instances its application is based on the fact that sulphurous anhydride acts on certain vegetable matters, and has the property of a reducing and feeble

[30] CH_4 gives CH_4O or $CH_3(OH)$, wood spirit; CH_4O_2 or $CH_2(OH)_2$, which decomposes into water and CH_2O—that is, methylene oxide or formaldehyde; $CH_4O_3 = CH(OH)_3 = H_2O + CHO(OH)$, or formic acid and $CH_4O_4 = C(OH)_4 = 2H_2O + CO_2$. There are four typical hydrogen compounds, RH, RH_2, RH_3, and RH_4, and each of them has its typical oxide. Beyond H_4 and O_4 combination does not proceed.

[31] Rhombic sulphur, 71080 heat units; monoclinic sulphur, 71720 units, according to Thomsen.

acid. For these purposes it is prepared by burning sulphur or iron pyrites, FeS_2.[32]

In the laboratory—that is, on a small scale—sulphurous anhydride is best prepared by deoxidising sulphuric acid by heating it with charcoal, or copper, sulphur, mercury, &c. Charcoal produces this decomposition of sulphuric acid at but moderately high temperatures; it is itself converted into carbonic anhydride, and therefore when sulphuric acid is heated with charcoal it evolves a mixture of sulphurous and carbonic anhydrides: $C+2H_2SO_4=CO_2+2SO_2+2H_2O$. The metals which are unable to decompose water, and which do not, therefore, evolve hydrogen from sulphuric acid, are frequently capable of decomposing sulphuric acid, with the evolution of sulphurous anhydride, just as they decompose nitric acid, forming the lower oxides of nitrogen. These metals are silver, mercury, copper, lead, and others. Thus, for example, the action of copper on sulphuric acid may be expressed by the following equation: $Cu+2H_2SO_4=CuSO_4+SO_2+2H_2O$. In the laboratory this reaction is carried on in a flask with a gas-conducting tube, and does not proceed unless aided by heat.[33]

[32] Sulphurous anhydride is also obtained by the decomposition of many sulphates, especially of the heavy metals, by the action of heat; but this requires a very powerful heat. This formation of sulphurous anhydride from sulphates is based on the decomposition proper to sulphuric acid itself. When sulphuric acid is powerfully heated (for instance, by dropping it upon an incandescent surface) it is decomposed into water, oxygen, and sulphurous anhydride—that is, into those compounds from which it is formed. A like decomposition proceeds during the ignition of many sulphates. In this case an oxide of the metal, oxygen, and sulphurous anhydride are formed. Even so stable a sulphate as gypsum does not resist the action of very high temperatures, but is decomposed in the same manner, lime being left behind. The decomposition of sulphates by heat is accomplished with still greater facility in the presence of sulphur, because in this case the liberated oxygen combines with the sulphur and the metal is able to form a sulphide. Thus when ferrous sulphate (green vitriol) is ignited with sulphur, it gives ferrous sulphide and sulphurous anhydride: $FeSO_4+2S=FeS+2SO_2$, and this reaction may even be used for the preparation of this gas. At 400° sulphuric acid and sulphur give an extremely uniform stream of pure sulphurous anhydride, so that it is best prepared on a large scale at works by this method. Iron pyrites, FeS_2, when heated to 150° with sulphuric acid (sp. gr. 1·75) in cast-iron vessels also gives an abundant and uniform supply of sulphurous anhydride.

[33] This reaction is connected with thermochemical data in the following manner. A molecule of hydrogen, H_2, in combining with oxygen (O=16) develops about 69000 heat units, whilst the molecule of SO_2 in combining with oxygen only develops about 32000 heat units—that is, about half as much—and therefore those metals which cannot decompose water are still able to deoxidise sulphuric into sulphurous acid. Those metals which decompose water and sulphuric acid with the evolution of hydrogen, evolve in combining with sixteen parts by weight of oxygen nearly as much if not more heat than hydrogen—for example, K_2,Na_2,Ca develop about or more than 100000 heat units; Fe, Zn, Mn about 70000 to 80000 heat units; whilst those metals which neither decompose water nor evolve hydrogen from sulphuric acid, but are yet capable of evolving sulphurous anhydride from it, develop less heat with oxygen than hydrogen, but nearly the same amount, if not more, than sulphurous anhydride—for example, Cu and Hg develop about 40000, and Pb about

In its physical and chemical properties sulphurous anhydride presents a great *resemblance to carbonic anhydride*. It is a heavy gas, somewhat considerably soluble in water, very easily condensed into a liquid; it forms normal and acid salts, does not evolve oxygen under the direct action of heat,[34] although such metals as sodium and magnesium burn in it, just as in carbonic anhydride. It has a suffocating odour, which is well known, owing to its being evolved when sulphur or sulphur matches are burnt. In characterising the properties of sulphurous anhydride, it is very important to remember (Chapter II.), also, that it is more easily liquefied (at $-10°$, or at $0°$ under two atmospheres pressure) than carbonic anhydride (thirty-six atmospheres at $0°$),[35] that it is more soluble than carbonic anhydride (Vol. I. p. 78) (namely at $0°$, 100 vols. of water dissolve 180 vols. of carbonic anhydride and 688 vols. of sulphurous anhydride), that the molecular weight of $SO_2=64$ and of $CO_2=44$, the density of liquid sulphurous anhydride at $0°=1{\cdot}43$ (molecular volume $=45$) and that of carbonic anhydride $=0{\cdot}95$ (molecular volume $=49$). The resemblance of the physical properties of carbonic and sulphurous anhydrides is also expressed in the great resemblance of the chemical characters of both anhydrides. Although sulphur dioxide is the anhydride of an acid, nevertheless, like carbonic anhydride, it does not form any stable compounds with water, but gives a solution from which it may be entirely expelled by the action of heat.[36] The acid character of sulphurous anhydride is clearly expressed by the fact that it is entirely absorbed by alkalis, with which it forms acid and normal salts easily soluble in water. With salts of barium, calcium, and the heavy metals, the normal salts of the alkalis, M_2SO_3, give precipitates exactly like those formed by the carbonates. In general, the salts of sulphurous acid are closely analogous to the corresponding carbonates.

50000, heat units. Naturally the affinity of the metallic oxide formed for the remaining sulphuric acid plays a part in the decomposition; and, as usual in thermochemical data, the experimental figure is complex, but still the general connection between the thermochemical phenomenon and the course of the reaction is evident.

[34] That is, it only dissociates and re-forms the original product on cooling.

[35] May not this be the reason why sulphurous anhydride has a more distinctly acid character? At a given temperature the pressure of this gas in any salt will be less than that of carbonic anhydride, if we compare the separation of a gas from its salts with the phenomenon of evaporation, as was pointed out in the decomposition of calcium carbonate.

Liquid sulphurous anhydride is used on a large scale (Pictet) for the production of cold.

[36] De la Rive, Pierre, and more especially B. Roozeboom, have investigated the crystallo-hydrate which is formed by sulphurous anhydride and water at temperatures below 7° under the ordinary pressure, and in closed vessels (at temperatures below 12). Its composition is $SO_2,7H_2O$, and density 1·2. This hydrate corresponds with the similar hydrate $CO_2,8H_2O$ obtained by Wroblewsky.

Acid sodium sulphite, $NaHSO_3$, may be obtained by passing sulphurous anhydride into a solution of sodium hydroxide. It is also formed by saturating a solution of sodium carbonate with the gas (carbonic anhydride is then given off), and as the solubility of the acid sulphite is much greater than that of the carbonate, a further quantity of the latter may be dissolved after the passage of the sulphurous anhydride, so that ultimately a very strong solution of the sulphite may be formed in this manner, from which it may be obtained in a crystalline form, either by cooling and evaporating (without heating, for otherwise the salt will give off sulphurous anhydride) or by adding alcohol to the solution. When exposed to the air this salt loses sulphurous anhydride and attracts oxygen, which converts it into sodium sulphate. The acid sulphites of the alkali metals are not only able to combine with oxygen, but also with many other substances—for example, a solution of the sodium salt dissolves sulphur, forming sodium thiosulphate, gives crystalline compounds with the aldehydes and ketones, and dissolves many bases, converting them into double sulphites. Having the faculty of attracting or absorbing oxygen, acid sodium sulphite is also able to absorb chlorine, and is therefore employed, like sodium thiosulphate, for the removal of chlorine (as an antichlor), especially in the bleaching of fabrics, when it is necessary to remove the last traces of the chlorine held in the tissues, which might otherwise have an injurious effect on them. If a solution of an alkali hydroxide be divided into two parts, and one half is saturated with sulphurous anhydride, and then the other half added to it, a normal salt will be obtained in the solution, having an alkaline reaction, like a solution of sodium carbonate. The acid salt has a neutral reaction. Like sodium carbonate, *normal sodium sulphite* has the composition $Na_2SO_3,10H_2O$, and its maximum solubility is at 33°—in a word, it very closely resembles sodium carbonate. Although this salt does not give off sulphurous anhydride from its solution, it is able, like the acid salt, to absorb oxygen from the air, and is then converted into sodium sulphate.[37]

Besides the acid character we must also point out the reducing character of sulphurous anhydride. *The reducing action* of sulphurous acid, its anhydride and salts, is due to their faculty of passing into sulphuric acid and sulphates. The reducing action of the sulphites is particularly energetic, so that they even convert nitric oxide into

[37] The normal salts of calcium and magnesium are slightly, and the acid salts easily, soluble in water. These acid sulphites are much used in practice; thus calcium bisulphite is employed in the manufacture of cellulose from sawdust, for mixing with fibrous matter in the manufacture of paper.

nitrous oxide: $K_2SO_3 + 2NO = K_2SO_4 + N_2O$. The salts of many of the higher oxides are converted into those of the lower—for example, FeX_3 into FeX_2, CuX_2 into CuX, HgX_2 into HgX; thus $2FeX_3 + SO_2 + 2H_2O = 2FeX_2 + H_2SO_4 + 2HX$. In the presence of water, sulphurous anhydride is oxidised by chlorine ($SO_2 + 2H_2O + Cl_2 = H_2SO_4 + 2HCl$), iodine, nitrous acid, hydrogen peroxide, hypochlorous acid, chloric acid, and other oxygen compounds of the halogens, chromic, manganic, and many other metallic acids and higher oxides, as well as all peroxides. Free oxygen in the presence of spongy platinum is able to oxidise sulphurous anhydride even in the absence of water, in which case sulphuric anhydride SO_3 is formed, so that the latter may be prepared by passing a mixture of sulphurous anhydride and oxygen over incandescent spongy platinum, or, as it is now prepared on a large scale in chemical works, by passing this mixture over asbestos or pumice stone moistened with a solution of platinum salt and ignited. Sulphurous anhydride is completely absorbed by certain higher oxides—for instance, by barium peroxide and lead dioxide ($PbO_2 + SO_2 = PbSO_4$).[38]

There are, however, cases when sulphurous anhydride acts as an oxidising agent—that is, it is *deoxidised* in the presence of substances which are capable of absorbing oxygen with still greater energy than the sulphurous anhydride itself. This oxidising action proceeds with the formation of sulphuretted hydrogen or of sulphides, while the reducing agent is oxidised at the expense of the oxygen of the sulphurous anhydride. In this respect, the action of stannous salts is particularly remarkable. Stannous chloride, $SnCl_2$, in an aqueous solution gives a precipitate of stannic sulphide, SnS_2, with sulphurous anhydride—that is, the latter is deoxidised to sulphuretted hydrogen. A solution of sulphurous anhydride has also an oxidising action on zinc. The zinc passes into solution, but no hydrogen is evolved,[39] because a

[38] This reaction is taken advantage of in removing sulphurous anhydride from a mixture of gases. Lead dioxide, PbO_2, is brown, and when combined with sulphurous anhydride it forms lead sulphate, $PbSO_4$, which is white, so that the reaction is evident both from the change in colour and development of heat. Sulphurous anhydride is slowly decomposed by the action of light, with the separation of sulphur and formation of sulphuric anhydride. This explains the fact that sulphurous anhydride prepared in the dark gives a white precipitate of silver sulphite, Ag_2SO_3, with silver chlorate, $AgClO_4$, but when prepared, even in diffused light, it gives a dark precipitate. This naturally depends on the fact that the sulphur liberated then forms silver sulphide, which is black.

[39] Schönebein observed that the liquid turns yellow, and acquires the faculty of decolorising litmus and indigo. Schützenberger showed that this depends on the formation of a zinc salt of a peculiar and very powerfully-reducing acid, for with cupric salts the yellow solution gives a red precipitate of cuprous hydride or metallic copper, and it reduces salts of silver and mercury entirely. An exactly similar solution is obtained by the action of zinc on sodium bisulphite without access of air and in the cold. The

salt of *hyposulphurous acid*, $Zn_2S_2O_4$, is formed. The free acid is still less stable than the salt.

The faculty of sulphurous anhydride of combining with various substances is evident from the above-cited reactions, where it combines with hydrogen and with oxygen, and this faculty also appears in the fact that, like carbonic oxide, it combines with chlorine, forming a chloranhydride of sulphuric acid, SO_2Cl_2, to which we shall afterwards return. The same faculty for combination also appears in the salts of sulphurous acid, in their liability to oxidation and in the exceedingly characteristic formation of a peculiar series of salts obtained by Pelouze and Frémy. At a temperature of $-10°$ or below, nitric oxide is absorbed by alkaline solutions of the alkali sulphites, forming a peculiar series of *nitrosulphates*. At a higher temperature, these salts are not formed, but the nitric oxide is reduced to nitrous oxide. But in the cold, the liquid saturated with nitric oxide after a certain time gives prismatic crystals resembling those of nitre. The composition of the potassium salt is $K_2SN_2O_5$—that is, the salt contains the elements of potassium sulphite and of nitric oxide.[40]

yellow liquid absorbs oxygen from the air with great avidity, and forms a sulphate. If the solution be mixed with alcohol, it deposits a double sulphite of zinc and sodium, $ZnNa_2(SO_3)_2$, which does not decolorise litmus or indigo. The remaining alcoholic solution deposits colourless crystals in the cold, which absorb oxygen with great energy in the presence of water, but are somewhat stable when dried under the receiver of an air-pump. When these crystals are oxidised in the presence of air and water they give sodium bisulphite. The solution of these crystals has the above-mentioned decolorising and reducing properties. These crystals contain a sodium salt of a lower acid; their composition was at first supposed to be $HNaSO_2$, but it was afterwards proved that they did not contain hydrogen, and present the composition $Na_2S_2O_4$ (Bernthsen). The same salt is formed by the action of a galvanic current on a solution of sodium bisulphite, owing to the action of the hydrogen at the moment of its liberation.

[40] The instability of this salt is very great, and may be likened to that of the compound of ferrous sulphate with nitric oxide, because when heated under the contact influence of spongy platinum, charcoal, &c., it splits up into potassium sulphate and nitrous oxide. At 130° the dry salt gives off nitric oxide, and re-forms potassium sulphite. The free acid has not yet been obtained. These salts resemble the series of *sulphonitrites* discovered by Frémy in 1845. They are obtained by passing sulphurous anhydride through a strong and highly alkaline aqueous solution of potassium nitrite. They are soluble in water, but are precipitated by an excess of alkali. The first product of the action has the composition $K_3NS_3HO_9$. It is then converted by the further action of sulphurous anhydride, cold water, and other reagents into a series of similar complex salts, many of which give well-formed crystals. One must suppose that the chief cause of the formation of these very complex compounds is that they contain unsaturated compounds, NO, KNO_2, and $KHSO_3$, all of which are subject to oxidation and further combination, and therefore easily combine among each other. The decomposition of these compounds, with the evolution of ammonia, when their solutions are heated is due to the fact that the molecule contains the deoxidant, sulphurous anhydride (Vol. I. p. 258), which reduces the nitrous acid, NO(OH), to ammonia. In my opinion the composition of the sulphonitrites may be very simply referred to the composition of ammonia, in which the hydrogen is partly replaced by the radicle of the sulphates. If we represent the compo-

There are yet several other substances, formed by the oxides of nitrogen and sulphur, which belong to this class of complex and, under some circumstances, unstable compounds. In the manufacture of sulphuric acid, both these classes of oxides come into contact with each other in the lead chambers, and if there be insufficient water for the formation of sulphuric acid they give crystalline compounds, termed *chamber crystals*. As a rule, the composition of the crystals is expressed by the formula $NHSO_5$. This is a compound of the radicles, NO_2, of nitric acid and, HSO_3, of sulphuric acid, or nitrosulphuric acid, $NO_2{\cdot}SHO_3$, if sulphuric acid be expressed as $OH{\cdot}SHO_3$ and nitric by $NO_2{\cdot}OH$. The tabular crystals of this substance fuse at about 70°, are formed both by the direct action of nitrous anhydride or nitric peroxide on sulphuric acid (Weltzen and others), and especially on sulphuric acid containing anhydride—for example, by means of the lower oxides of nitrogen and the higher oxides of sulphur—and also by the action of the lower oxides of sulphur and nitric acid.[41]

sition of potassium sulphate as $KO{\cdot}KSO_3$, then the group KSO_3 will be equivalent (according to the law of substitutions) to HO and to hydrogen. It combines with hydrogen, forming the potassium acid sulphite, $KHSO_3$. Therefore the group KSO_3 may also replace the hydrogen in ammonia. Judging by my analysis (1870) the extreme limit of this substitution, $N(HSO_3)_3$, agrees with that of the sulpho-nitrite, which is easily formed, simultaneously with alkali, by the action of potassium sulphite on potassium nitrite, according to the equation $3K(KSO_3)+KNO_2+2H_2O=N(KSO_3)_3+4HKO$. The researches of Berglund, and especially of Raschig (1887), fully verified my conclusions, and showed that we must distinguish the following types of salts, corresponding with ammonia, where X stands for the sulphonic group, HSO_3, in which the hydrogen is replaced by potassium; hence $X=KSO_3$: (1) NH_2X, (2) NHX_2, (3) NX_3, (4) $N(OH)XH$, (5) $N(OH)X_2$, (6) $N(OH)_2X$, just as $NH_2(OH)$ is hydroxylamine, $NH(OH)_2$ is the hydrate of nitrous oxide, and $N(OH)_3$ is orthonitrous acid, as follows from the law of substitutions. This class of compounds is in most intimate relation with the series of sulphonitrous compounds, corresponding with 'chamber crystals' and their acids, which we shall consider later.

[41] In the sulphuric acid chambers the lower oxides of nitrogen and sulphur take part in the reaction. They are oxidised by the oxygen of the air, and form nitro-sulphuric acid—for example, $2SO_2+N_2O_3+O_2+H_2O=2NHSO_5$. This compound dissolves in strong sulphuric acid without changing, and when this solution is diluted (when the sp. gr. falls to 1·5) it splits up into sulphuric acid and nitrous anhydride, and by the action of sulphurous anhydride is converted into nitric oxide, which by itself (in the absence of nitric acid or oxygen) is insoluble in sulphuric acid. These reactions are taken advantage of in retaining the oxides of nitrogen in the Gay-Lussac coke-towers, and for extracting the absorbed oxides of nitrogen from the resultant solution in the Glover's tower (Vol. I. p. 284). Although nitric oxide is not absorbed by sulphuric acid, it reacts (Rose, Brüning) on its anhydride, and forms sulphurous anhydride and a crystalline substance, $N_2S_2O_9=2NO+3SO_3-SO_2=N_2O_3{\cdot}2SO_3$. This may be regarded as the anhydride of nitro-sulphuric acid, because $N_2S_2O_9=2NHSO_5-H_2O$; like nitro-sulphuric acid, it is decomposed by water into nitro-sulphuric acid and nitrous anhydride. Since boric and arsenious anhydrides, alumina and other oxides of the form R_2O_3 are able to combine with sulphuric anhydride to form similar compounds decomposable by water, the above compound does not present any exceptional phenomenon.

Thiosulphuric acid, $H_2S_2O_3$—that is, a compound of sulphurous acid and sulphur—also belongs to the products of combination of sulphurous acid. In a free state it is very unstable and it is only known in the form of its salts proceeding from the direct action of sulphur on the normal sulphites; if endeavours be made to separate it in a free state, it immediately splits up into those elements from which it might be formed—that is, into sulphur and sulphurous acid. The most important of its salts is the *sodium thiosulphate*, $Na_2S_2O_3,5H_2O$, which occurs in colourless crystals, which are unacted on by atmospheric oxygen either when in a dry state or in solution. Many other salts of this acid are easily formed by means of this salt, although this cannot be done with all bases, for such bases as alumina, ferric oxide, chromium oxide, and others do not give compounds with thiosulphuric acid, just as they do not form stable compounds with carbonic acid. Whenever these salts might be formed, they (like the acid) split up into sulphurous acid and sulphur, and furthermore the elements of thiosulphuric acid in many cases act in a reducing manner, forming sulphuric acid and taking up the oxygen from reducible oxides. Thus, when treated with a thiosulphate the soluble ferric salts give a precipitate of sulphur and form ferrous salts, in which case it is the elements of sulphurous acid which act: $H_2S_2O_3=SO_2+S+H_2O$. The thiosulphates of the metals of the alkalis are obtained directly by boiling a solution of their sulphites with sulphur: $Na_2SO_3+S=Na_2S_2O_3$. The same salts are formed by the action of sulphurous anhydride on solutions of the sulphides: thus, sodium sulphide dissolved in water gives sulphur and sodium thiosulphate, when a stream of sulphurous anhydride is passed through it: $2Na_2S+3SO_2=2Na_2S_2O_3+S$. The polysulphides of the alkali metals when left exposed to the air attract oxygen and also form thiosulphates.[42]

[42] Thus when alkali waste, which contains calcium sulphide, undergoes oxidation in the air it first forms a calcium polysulphide, and then calcium thiosulphate, CaS_2O_3. If iron or zinc acts on a solution of sulphurous acid, then, besides the hyposulphurous acid first formed, a mixture of sulphite and thiosulphate is obtained. Thus, for example, with zinc, $3SO_2+Zn_2=ZnSO_3+ZnS_2O_3$. In this case, as in the formation of hyposulphurous acid, there is no hydrogen liberated. One of the most common methods for preparing thiosulphates consists in the *action of sulphur on the alkalis*. The reaction is accompanied by the formation of sulphides and thiosulphates, just as the reaction of chlorine on alkalis is accompanied by the formation of hypochlorites and chlorides; hence in this respect the thiosulphates hold the same position in the order of the compounds of sulphur as the hypochlorites do among the chlorine compounds. The reaction of caustic soda on an excess of sulphur may be expressed thus: $6NaHO+12S=2Na_2S_5+Na_2S_2O_3+3H_2O$. Thus sulphur is soluble in alkalis. On a large scale sodium thiosulphate, $Na_2S_2O_3$, is prepared by first heating sodium sulphate with charcoal, to form sodium sulphide, which is then dissolved in water and treated with sulphurous anhydride. The reaction is completed when the solution becomes slightly acid. A certain amount of caustic alkali is

Although sulphur, in combining directly with oxygen, only forms a small quantity of sulphuric anhydride, SO_3, and nearly all passes into sulphurous anhydride, still the latter may be converted into the higher oxide, or *sulphuric anhydride*, SO_3, by many methods. Sulphuric anhydride is a solid crystalline substance at the ordinary temperature; it is easily fusible (16°), and volatile, and attracts moisture with great

added to the slightly acid solution; a portion of the sulphur is thus precipitated, and the solution is then boiled and evaporated in order to crystallise out the salt. The saturation of the solution of sodium sulphide by sulphurous anhydride is carried on in different ways—for example, by means of coke towers, by causing the solution of sulphide to trickle over the coke, and the sulphurous anhydride, obtained by burning sulphur, to pass up the coke tower from below. An excess of sulphurous anhydride must be avoided, as otherwise sodium trithionate is formed. Sodium thiosulphate is also prepared by the double decomposition of the soluble calcium thiosulphate with sodium sulphate or carbonate, in which case calcium sulphate or carbonate is precipitated. The calcium thiosulphate is prepared by the action by sulphurous anhydride on either calcium sulphide or alkali waste. A dilute solution of calcium thiosulphate may be obtained by treating alkali waste which has been exposed to the action of air with water. On evaporation, this solution gives crystals of the salt containing 5 molecules H_2O. A solution of calcium thiosulphate must be evaporated with great care, because otherwise the salt breaks up into sulphur and calcium sulphide. Even the crystallised salt sometimes undergoes this change.

The crystals of sodium thiosulphate are stable, do not effloresce, and at 0° dissolve in one part of water, and at 20° in 0·6 part. The solution of this salt does not undergo any change when boiled for a short time, but after prolonged boiling it deposits sulphur. The crystals fuse at 56°, and lose all their water at 100°. When the dry salt is ignited it gives sodium sulphide and sulphate. With acids, a solution of the thiosulphate soon becomes cloudy and deposits an exceedingly fine powder of sulphur. If the amount of acid added be considerable it also evolves sulphurous anhydride, owing to the instability of the hyposulphurous acid itself: $H_2S_2O_3 = H_2O + S + SO_2$. Sodium thiosulphate has many practical uses; it is used in photography for dissolving silver chloride and bromide. Its solvent action on silver chloride may be taken advantage of in extracting this metal as chloride from its ores. In dissolving, it forms a double salt of silver and sodium: $AgCl + Na_2S_2O_3 = NaCl + AgNaS_2O_3$. Sodium thiosulphate is an *antichlor*—that is, a substance which hinders the destructive action of free chlorine owing to its being very easily oxidised by chlorine into sulphuric acid and sodium chloride. The reaction with iodine is different, and is remarkable for the accuracy with which it proceeds. The iodine takes up half the sodium from the salt and converts it into a tetrathionate; $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$. Hence a solution of sodium thiosulphate may be employed for the determination of free iodine. As iodine is expelled from potassium iodide by chlorine, it is possible also to determine the amount of chlorine by this method if potassium iodide be added to a solution containing chlorine. And as many of the higher oxides are able to evolve iodine from potassium iodide, or chlorine from hydrochloric acid (for example, the higher oxides of manganese, chromium, &c.), it is also possible to determine the amounts of these higher oxides by means of sodium thiosulphate and liberated iodine. The details of these methods must be looked for in books on analytical chemistry.

On adding a solution of a *lead salt* gradually to a solution of sodium thiosulphate, there is formed a white precipitate of lead thiosulphate, PbS_2O_3 (at first in this reaction a soluble double salt, and if the action be rapid, lead sulphide). When this substance is heated at 200°, it undergoes a change and takes fire. Sodium thiosulphate in solution soon reduces the cupric salts into cuprous salts by means of the sulphurous acid contained in the thiosulphate, but the resultant cuprous oxide is not precipitated, because it passes into the state of a thiosulphate and forms a double salt with the hyposulphite taken. These double cuprous

energy. Although it is formed by the combination of sulphurous anhydride with oxygen, it is liable to further combination. Thus it combines with water, hydrochloric acid, ammonia, with many hydrocarbons, and even with sulphuric acid, boric and nitrous anhydrides, &c., not to mention bases which burn directly in its vapour, forming sulphates. The oxidation of sulphurous anhydride, SO_2, into sulphuric anhydride, SO_3, is accomplished by passing a mixture of the former and dry oxygen or air over incandescent spongy platinum, by means of which a combination takes place between the two gases. An increase of pressure accelerates the reaction (Hänisch). If the product be passed into a cold vessel, crystalline sulphuric anhydride is deposited upon the sides of the vessel, but as it is difficult to avoid all traces of moisture it always contains compounds of its hydrates: $H_2S_2O_7$ and $H_2S_4O_{13}$, whose presence so modifies the properties of the anhydride (Weber) that formerly two modifications of the anhydride were recognised (Marignac, Schultz-Sellack, and others). The same (an impure but perfectly anhydrous anhydride is formed by distilling over phosphoric anhydride) sulphuric anhydride may be obtained from certain anhydrous, or almost so, sulphates, which are decomposed by heat. Such are, for instance, the acid sodium sulphate, $NaHSO_4$, and the pyro- or di-sulphate, $Na_2S_2O_7$ (Vol. I. p. 510), formed from it, which when ignited evolve sulphuric anhydride; also ferrous sulphate, and certain other salts which are easily decomposed by the action of heat. If the sulphate taken decomposes at a very high temperature, sulphuric anhydride is not obtained, but is split up into oxygen and sulphurous anhydride. Green vitriol—that is, ferrous sulphate, $FeSO_4$—belongs to the number of those sulphates which easily give off sulphuric anhydride. It contains water of crystallisation, and parts with it when it is heated, but the last equivalent of water is driven off with difficulty, just as is the case with magnesium sulphate; however, under the action of a powerful heat this evolution of sulphuric anhydride does take place,

salts are excellent reducing agents. The solution becomes colourless on the formation of cuprous salts, and when heated it gives a black precipitate of copper sulphide.

The following formulæ sufficiently explain the position held by thiosulphuric acid among the other acids of sulphur:

Sulphurous acid	$SO_2H(OH)$
Sulphuric acid	$SO_2OH(OH)$
Thiosulphuric acid	$SO_2SH(OH)$
Hyposulphurous acid	$SO_2H(SO_2H)$
Dithionic acid	$SO_2OH(SO_2OH)$

At one time it was thought that all the salts of thiosulphuric acid only existed with water, and it was then supposed that their composition was $H_4S_2O_4$, or H_2SO_2, but Popp obtained the anhydrous salts.

although not completely, because at a high temperature a portion of it is decomposed by the ferrous oxide ($SO_3 + 2FeO$), which is converted into ferric oxide, Fe_2O_3, and in consequence a portion of the sulphuric anhydride is converted into sulphurous anhydride. Thus the products of the decomposition of ferrous sulphate will be: ferric oxide, Fe_2O_3, sulphurous anhydride, SO_2, and sulphuric anhydride, SO_3, according to the equation: $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$. As water still remains with the ferrous sulphate when it is heated, the result will partially consist of the hydrate H_2SO_4, with anhydride, SO_3, dissolved in it. Sulphuric acid was for a long time prepared in this manner; this process was formerly carried on on a large scale in the neighbourhood of Nordhausen, and, therefore, the sulphuric acid prepared from ferrous sulphate is called *fuming Nordhausen acid.* At the present time the fuming acid is prepared by passing the volatile products of the decomposition of ferrous sulphate through strong sulphuric acid prepared by the ordinary method. The sulphurous anhydride is insoluble in it, but it absorbs the sulphuric anhydride. Sulphuric anhydride may be better prepared by igniting a mixture of sodium pyrosulphate, $Na_2S_2O_7$, and magnesium sulphate (Walters; the decomposition proceeds at 600°) than from ferrous sulphate or sodium pyrosulphate alone; because in the former case there remains a stable double salt $MgNa(SO_4)_2$. Nordhausen sulphuric acid fumes in air, owing to its containing and easily giving off sulphuric anhydride, and it is therefore also called *fuming sulphuric acid;* these fumes are nothing but the vapour of sulphuric anhydride combining with the moisture in the air, and forming non-volatile sulphuric acid (hydrate).[43]

Nordhausen sulphuric acid as a solution of sulphuric anhydride in

[43] Nordhausen sulphuric acid may serve as a very simple means for the preparation of sulphuric anhydride. For this purpose the Nordhausen acid is heated in a glass retort, whose neck is firmly fixed in the mouth of a well-cooled flask. The access of moisture is prevented by connecting the receiver with a drying tube. On heating the retort the vapours of the volatile sulphuric anhydride will pass over into the receiver, where they condense; the anhydride thus prepared will, however, contain traces of sulphuric acid—that is, of the hydrate—because it rapidly attracts moisture from the air and forms sulphuric acid. By repeatedly distilling over phosphoric anhydride, it is possible to obtain the pure anhydride, SO_3, especially if the process be carried on without access of air.

The ordinary sulphuric anhydride, which is imperfectly freed from the hydrate, is a snow-white, exceedingly volatile substance; it fuses at 16° into a colourless liquid having a specific gravity at 26° = 1·91, and at 47° = 1·81; it volatilises at 46°. After being kept for some time this substance undergoes a change, a small quantity of sulphuric acid combining by degrees with a large proportion of the anhydride, forming polysulphuric acids, H_2SO_4, nSO_3, which fuse with difficulty (even at 100°, Marignac), but decompose when heated. In the entire absence of water this rise in the fusing point does not occur (Weber), and then the anhydride long remains liquid, and solidifies at about +15°, volatilises at 40°, and has a specific gravity 1·94 at 16°.

sulphuric acid contains a peculiar compound of these substances, or *pyrosulphuric acid*; an imperfect anhydride of sulphuric acid, $H_2S_2O_7$, analogous in composition with the salts, $Na_2S_2O_7$, $K_2Cr_2O_7$, and similar pyro-salts or anhydro-acid salts. At all events the bond holding the sulphuric acid and anhydride together is unstable. This is obvious from the fact that the anhydride may easily be separated from this compound by the action of heat. In order to obtain the definite compound, the Nordhausen acid is cooled to 5°, or, better still, a portion of it is distilled until all the anhydride and a certain amount of sulphuric acid have passed over into the distillate, which will then solidify at the ordinary temperature, because the compound H_2SO_4,SO_3 fuses at 35°. Although this substance reacts on water, bases, &c., like a mixture of $SO_3+H_2SO_4$, still as a definite compound, $H_2S_2O_7$, exists in a free state and gives salts and a chloranhydride, $S_2O_5Cl_2$,[44] we must admit the existence of a particular pyrosulphuric acid, like pyrophosphoric acid, remarking only that the latter imperfect anhydride has a far greater stability and is not even converted into a perfect hydrate by water. Further, the salts $M_2S_2O_7$ dissolved in water react in the same manner as the acid salts $MHSO_4$, whilst the imperfect hydrates of phosphoric acid (for example, PHO_3, $H_4P_2O_7$) have independent reactions even in an aqueous solution which distinguish them and their salts from the perfect hydrates.

Sulphuric acid, H_2SO_4, is formed by the combination of its anhydride, SO_3, and water, with the evolution of a large amount of heat; the reaction SO_3+H_2O develops 21300 heat units. The methods of its preparation on a larger scale, as well as the majority of known

[44] Pyrosulphuric chloranhydride, or *pyrosulphuryl chloride*, $S_2O_5Cl_2$, corresponds with pyrosulphuric acid, in the same way that sulphuryl chloride, SO_2Cl_2, corresponds with sulphuric acid. The composition $S_2O_5Cl_2 = SO_2Cl_2+SO_3$. It is obtained by the action of the vapour of sulphuric anhydride on sulphur chloride: $S_2Cl_2+5SO_3=5SO_2+S_2O_5Cl_2$. It is also formed (and not sulphuryl chloride, SO_2Cl_2, Michaelis) by the action of phosphorus pentachloride in excess on sulphuric acid (or its first chloranhydride, SHO_3Cl). It is an oily liquid, boiling at about 150°, and of sp. gr. 1·8. According to Konovaloff (Vol. I. p. 314), its vapour density is normal. It should be noticed that the same substance is obtained by the action of sulphuric anhydride on sulphur tetrachloride, and also on carbon tetrachloride, and this substance is the last product of the metalepsis of CH_4, and therefore the comparison of SCl_2 and S_2Cl_2 with products of metalepsis (see further) also finds confirmation in particular reactions. Rose, who obtained pyrosulphuryl chloride, $S_2O_5Cl_2$, regarded it as $SCl_6,5SO_3$, for at that time they always endeavoured to find two component parts of opposite polarity. And then the substance in question was cited as a proof of the existence of a hexacliloride, SCl_6. Pyrosulphuryl chloride is decomposed by cold water, but more slowly than chlorosulphuric acid, and the other chloranhydrides.

The relation between pyrosulphuric acid and the normal acid will be obvious if we express the latter by the formula $OH(SO_3H)$, because the sulphonic group (SO_3H) is evidently equivalent to OH, and consequently to H, and therefore if we replace both the hydrogens in water by this radicle we shall obtain $(SO_3H)_2O$—that is, pyrosulphuric acid.

methods for its formation, are dependent on the oxidation of sulphurous anhydride, and the formation of sulphuric anhydride, which forms sulphuric acid under the action of water. The technical mode of its manufacture has been described in Chap. VI., Vol. I. p. 284. The acid obtained *from the lead chambers* is diluted with a considerable amount of water, and is also impure, owing to the presence of oxides of nitrogen, lead compounds, and certain impurities from the burnt sulphur which have come over in a gaseous and vaporous state (for example, arsenic compounds). For practical purposes, hardly any notice is taken of the majority of these impurities, because they do not interfere in its general qualities. Most frequently endeavours are only made to remove, as far as possible, all the water which may be expelled without destroying the composition of sulphuric acid as a hydrate.[45] That is, the object is to obtain the hydrate, H_2SO_4, from the dilute acid. The separation of the water from the dilute acid is carried on by evaporating with the aid of heat. Every given mixture of water and sulphuric acid begins to part with a certain amount of aqueous vapour when heated to a certain definite temperature. At a low temperature there is either no evaporation of water, or even an absorption of moisture from the air. As the removal of the water proceeds, the temperature at which it comes off rises; the more dilute the acid the lower the temperature at which it gives up a portion of its water. In consequence of this, the removal of water from dilute solutions of sulphuric acid may be easily carried on (up to 60° Baumé) in lead, and still better in glass, vessels, because at low temperatures dilute sulphuric acid does not corrode either glass or lead. But as the acid becomes more concentrated the temperature at which the water comes over becomes higher and higher, and then the acid begins to act on lead (with the evolution of sulphuretted hydrogen and conversion of the lead into sulphate), and therefore lead vessels cannot be employed for the entire removal of the water. For this purpose the evaporation is generally carried on in glass or platinum retorts, like those depicted in figs. 87 and 88.

The concentration of sulphuric acid in glass retorts is not a continuous process, and consists of heating the dilute acid until it ceases to give off aqueous vapour, and until the sulphuric acid itself begins to

[45] The removal of the water, or concentration to almost the real acid, H_2SO_4, is effected for two purposes: in the first place to avoid the expense of transit (it is cheaper to remove the water than to pay for its transit to a great distance), and in the second place many processes—for instance, the refining of petroleum—require a strong acid free from an excess of water, the weak acid having no action. On this account the production of sulphuric anhydride increases year by year, and probably in time it will be an important competitor to chamber acid.

come off—that is, until the composition of the residue is the same as that of the distillate—and this takes place when the temperature

FIG. 87.—Concentration of sulphuric acid in glass retorts. The neck of each retort is attached to a bent glass tube, whose vertical arm is lowered into a glass or earthenware vessel acting as a receiver for the steam which comes over from the acid, as the former still contains a certain amount of acid.

reaches 320° and the density of the residue 1·847 (=66° Baumé).[46] The platinum vessels designed for the continuous concentration of sulphuric

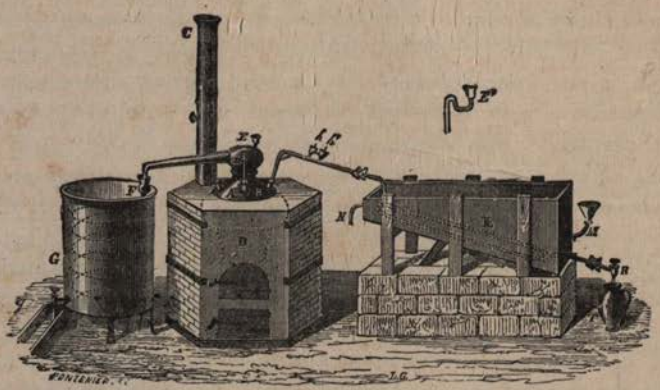


FIG. 88.—Concentration of sulphuric acid in platinum retorts.

acid consist of a boiler, B, furnished with a helmet, E, a vapour-conducting pipe, E F, and a syphon tube, H R, which draws off the sulphuric

[46] The difficulty with which the last portions of water are removed is seen from the fact that the boiling becomes very irregular, totally ceasing at one moment, then suddenly starting again, with the rapid formation of a considerable amount of steam, and at the

acid concentrated in the boiler. A stream of sulphuric acid previously concentrated in lead retorts to a density of about 60° Baumé—*i.e.* to a sp. gr. of 1·7—runs continuously into the retort through an upper funnel E. The apparatus is fed from above, because the acid freshly supplied is lighter than that which has already lost water, and also because the water is more easily evaporated from the freshly-supplied acid at the surface. The platinum retort is heated, and the steam coming off is condensed in a worm F G, whilst as fresh diluted acid is supplied to the boiler the acid already concentrated is drawn off through the syphon tube H B, which is furnished with a regulating cock, by means of which the outflow of the concentrated acid from the bottom of the retort can be so regulated that it will always present one and the same specific gravity, corresponding with the strength required. For this purpose, the acid flowing from the syphon is collected in a receiver R, in which a hydrometer, indicating its density, floats ; if its density be less than 66° Baumé, the regulating cock is closed sufficiently to retard the outflow of sulphuric acid, so as to lengthen the time of its evaporation in the retort.[47]

same time jerking and even overturning the vessel in which it is held. Hence it is not a rare occurrence for the glass retorts to break during the distillation; this causes platinum retorts to be preferred, as the boiling then proceeds quite uniformly.

[47] The greatest part of the sulphuric acid is used in the soda manufacture, in the conversion of the common salt into sulphate. For this purpose an acid having a density of 60° Baumé is amply sufficient. Chamber acid has a density up to 1·57 = 50° to 51° Baumé ; it contains about 85 per cent. of water. About 15 per cent. of this water can be removed in leaden stills, and nearly all the remainder may be expelled in glass or platinum vessels. Acid of 66° Baumé, =1·847, contains about 96 per cent. of the hydrate H_2SO_4. The density falls with a greater or less proportion of water, the maximum density corresponding with 97½ per cent. of the hydrate H_2SO_4.

When, by heating and evaporation of the water, sulphuric acid attains a density of 66° Baumé (sp. gr. 1·84), it is impossible to concentrate it further, because it then distils over unchanged. *The distillation of sulphuric acid* is not generally carried on on a large scale, but forms a laboratory process, employed when particularly pure acid is required. The distillation is effected either in platinum retorts furnished with corresponding condensers and receivers, or in glass retorts. In the latter case, great caution is necessary, because the boiling of sulphuric acid itself is accompanied by still more violent jerks and greater irregularity than even the evaporation of the last portions of water contained in the acid. If the glass retort which holds the strong sulphuric acid to be distilled be heated directly from below, it frequently jerks and breaks. For greater safety the heating is not effected from below, but at the sides of the retort. Then the evaporation does not proceed in the whole mass, but only from the upper portions of the liquid, and therefore goes on much more quietly. For this purpose the bottom of the retort is protected from the action of heat; for example, by immersing it in a special basin and lowering the bottom of the retort below the charcoal stove, by means of which the acid is heated. The acid may be made to boil quietly also by surrounding the retort with good conductors of heat—for example, iron filings, or by immersing a bunch of platinum wires in the acid, as the bubbles of sulphuric acid vapour then form on the extremities of the wires.

Strictly speaking, *sulphuric acid is not volatile*, and at its so-called boiling-point [48] it really decomposes into its anhydride and water; its boiling-point (338°) being nothing else but its temperature of decomposition. The products of this decomposition are substances boiling much below the temperature of the decomposition of sulphuric acid. This conclusion with regard to the process of the distillation of sulphuric acid may be deduced from Bineau's observations on the vapour density of sulphuric acid. This density referred to hydrogen proved to be half that which sulphuric acid should have according to its molecular weight, H_2SO_4, in which case it should be 49, whilst the observed density was equal to 24·5. Besides which, Marignac showed that the first portions of the sulphuric acid distilled over contain less of the elements of water than the portion which remains behind, or which distils over towards the end. This is explained by the fact that in distilling the sulphuric acid is decomposed, but a portion of the water proceeding from its decomposition is retained by the remaining mass of sulphuric acid, and therefore at first a mixture of sulphuric acid and sulphuric anhydride—*i.e.* fuming sulphuric acid—is obtained in the distillate. It is possible by repeating the distillation several times and only collecting the first portions of the distillate, to obtain a distinctly-fuming acid. To obtain the definite hydrate H_2SO_4, it is necessary to refrigerate a highly-concentrated acid, of as great a purity as possible, to which a small quantity of sulphuric anhydride has been previously added (because pure sulphuric acid does not separate in presence of a small quantity of water). Pure sulphuric acid, H_2SO_4, solidifies when it is cooled below 0°, and therefore the

[48] According to Regnault, the vapour tensions (in millimetres of mercury) of the vapour given off by the hydrates of sulphuric acid, H_2SO_4,nH_2O, are—

	$t=5°$	15°	30°
$n=1$	0·1	0·1	0·2
2	0·4	0·7	1·5
3	0·9	1·6	4·1
4	1·8	2·8	7·0
5	2·1	4·2	10·7
7	3·2	6·2	15·6
9	4·1	8·0	19·6
11	4·4	9·0	22·2
17	5·5	10·6	26·1

According to Lunge, the vapour tension of the aqueous vapour given off from solutions of sulphuric acid containing p per cent. H_2SO_4, at $t°$, equals the barometric pressure 720 to 730 mm.

$p=$	10	20	30	40	50	60	70	80	85	90	95
$t=$	102°	105°	108°	114°	124°	141°	170°	207°	238°	262°	295°

normal acid first crystallises out from the concentrated sulphuric acid. By repeating the refrigeration several times, and pouring off the unsolidified portion, it is possible to obtain a pure *normal hydrate*, H_2SO_4, which melts at 10°. The presence of several per cents. of water considerably lowers the freezing-point. At 40° it already gives off distinct fumes—that is, it begins to decompose into sulphuric anhydride, which volatilises, and water, which is absorbed by the remaining mass of sulphuric acid, and therefore even in a dry atmosphere the hydrate H_2SO_4 becomes weaker, until it attains a dilution of $1\frac{1}{2}$ p.c. of water. Thus it appears that so common, and apparently so stable, a compound as sulphuric acid decomposes even at a low temperature with separation of the anhydride, but this decomposition is restricted by a limit, corresponding to the presence of about $1\frac{1}{2}$ p.c. of water, or to a composition of nearly $H_2O,12H_2SO_4$.[49]

In a concentrated form sulphuric acid is commercially known as *oil of vitriol*, because for a long time it was obtained from green vitriol, and because it has an oily appearance and flows from one vessel into another in a thick and comparatively immobile stream, like the majority of oily substances, and in this clearly differs from such liquids as water, spirit, ether, and the like, which exhibit a far greater mobility. Among its properties, the first to be remarked is its faculty for the formation of many compounds. We already know that it combines with its anhydride, and with the sulphates of the alkali metals; that it is soluble in water, with which it forms more or less stable compounds. Sulphuric acid, when mixed with water, develops a very considerable amount of heat.[50]

[49] Now there is no reason for thinking that this substance is a definite compound; it is an equilibrated system which does not decompose under ordinary circumstances below 338°. Dittmar carried on the distillation under pressures varying between 30 and 2140 millimetres (of mercury), and he found that the composition of the residue hardly varies, and contains from 99·2 to 98·2 per cent. of the normal hydrate, although at 30 mm. the temperature of distillation is about 210° and at 2140 mm. it = 382°. Furthermore, it is a circumstance of practical importance that under a pressure of two atmospheres the distillation of sulphuric acid proceeds very quietly.

Sulphuric acid may be *purified* from the majority of its impurities by distillation, if the first and last portions of the distillate be rejected. The first portions will contain the oxides of nitrogen, hydrochloric acid, &c., and the last portions the less volatile impurities. The oxides of nitrogen may be removed by heating the acid with charcoal, which converts them into volatile gases. Sulphuric acid may be freed from arsenic by heating it with manganese dioxide and then distilling. This oxidises all the arsenic into non-volatile arsenic acid. Without a preliminary oxidation it would partially remain as volatile arsenious acid, and might pass over into the distillate. The arsenic may also be driven off by first reducing it to arsenious acid, and then passing hydrochloric acid gas through the heated acid. It is then converted into arsenious chloride, which volatilises.

[50] The amount of heat developed by the mixture of sulphuric acid with water is

Besides the normal hydrate H_2SO_4, *another definite hydrate* H_2SO_4,H_2O (84·48 per cent. of the normal hydrate, and 15·52 per cent. of water) is known; it crystallises extremely easily in large six-sided prisms, which form above 0°—namely, at about +8°; when heated to 210° it loses water.[51]

If the hydrates H_2SO_4 and H_2SO_4,H_2O exist at low temperatures as definite compounds, and if pyrosulphuric acid, $H_2SO_2SO_3$, has the same property, and if they all decompose with more or less ease on a rise of temperature, with the disengagement of either SO_3 or H_2O (and these elements of sulphuric acid are evolved quite separately from each other—that is, uncombined), then it follows that between sulphuric anhydride, SO_3, and water, H_2O, there exists an uninterrupted and consecutive series of homogeneous substances which in a liquid state are nothing else than solutions.

However, as among them we must distinguish the above-mentioned *definite compounds*, which are incapable of taking a vaporous form, but able to pass into a solid state, it is indispensable, in order to arrive at a right judgment, to seek for other means for determining the existence of any definite compounds—beyond the conditions for a change of state. In this respect we may be guided by the variation of properties of any kind, which proceeds with a variation in the composition of solutions. For definite compounds we should ex-

expressed by the diagram on p. 76, Vol. I., by the middle curve, whose abscissæ are the percentage amounts of acid (H_2SO_4) in the resultant solution, and ordinates the number of units of heat corresponding with the formation of 100 cubic centimetres of the solution (at 18°). The calculations on which the curve is designed are based on Thomsen's determinations, which show that 98 grams or a molecular amount of sulphuric acid, in combining with m molecules of water (that is, with m 18 grams of water), develop the following number of units of heat, R:—

m =	1	2	3	5	9	19	49	100	200
R =	6379	9418	11137	13108	14952	16256	16684	16859	17066
c =	0·432	0·470	0·500	0·576	0·701	0·821	0·914	0·954	0·975
T =	127°	149°	146°	121°	82°	45°	19°	9°	5°

c stands for the specific heat of $H_2SO_4 m H_2O$ (according to Marignac and Pfaundler), and T for the rise in temperature which proceeds from the mixture of H_2SO_4 with mH_2O. The diagram shows that contraction and rise of temperature proceed almost parallel with each other.

[51] With an excess of snow, the hydrate H_2SO_4,H_2O, like the normal hydrate, gives a freezing mixture, owing to the absorption of a large amount of heat (at the expense of the latent heat of fusion). In melting, the molecule H_2SO_4 absorbs 960 heat units, and the molecule $H_2SO_4H_2O$ 3680 heat units. If we mix, for example, one gram molecule of this hydrate with seventeen gram molecules of snow, then there is an absorption of 18080 heat units, because $17H_2O$ absorbs 17×1430 heat units, and the combination of the monohydrate with water evolves 9800 heat units. As the specific heat of the resultant compound $H_2SO_4,18H_2O = 0·813$, the fall of temperature will be = 52·6. And so in reality an extreme degree of cold may be obtained by means of sulphuric acid.

pect changes in properties, and this is observed to be the case in reality. But only a few properties have been determined with sufficient accuracy. In those properties which have been determined for many solutions of sulphuric acid, it is actually seen that the above-mentioned definite compounds are distinguished by distinctive marks of change. As an example we may cite the variation of the specific gravity with a variation of temperature (namely ds/dt, if s be the sp. gr. and t the temperature). For the normal hydrate, H_2SO_4, this factor ds/dt or k is easily determined from the fact that—

$$s=18528—10{\cdot}65t+0{\cdot}0013t^2,$$

where s is the specific gravity at t (degrees Celsius) if the sp. gr. of water at 4°=10000. Therefore, $k=10{\cdot}65—0{\cdot}026t$. This means that at 0° the sp. gr. of the acid H_2SO_4 decreases by 10·65 for every rise of a degree of temperature, at 10° by 10·39, at 20° by 10·13, at 30° by 9·87.[52] And for solutions containing slightly more anhydride than the acid H_2SO_4 (*i.e.* for fuming sulphuric acid), as well as for solutions containing little water, the magnitude $-k$ is greater than for the acid H_2SO_4. Thus for the solution $SO_3,2H_2SO_4$, at 10° $-k=10{\cdot}9$, and for the acid H_2SO_4 at 10°—$k=10{\cdot}4$. On diluting the acid H_2SO_4 this increase of the magnitude $-k$ goes on until the formation of the solution H_2SO_4,H_2O($-k=11{\cdot}1$ at 10°), and then, on the further dilution with water, it again decreases. Consequently both hydrates H_2SO_4 and H_2SO_4,H_2O are here expressed by an alteration of the magnitude of K.

Of all the properties of the solutions of sulphuric acid, the specific gravity has been the most thoroughly investigated. The researches of Bineau, Kremers, Lunge and Naef, Marignac, Mendeléeff, Ostwald, Schertel and Winkler, give the following specific gravities (in a vacuum ; water 4°=10000) at 0°.[53]

		H_2O	s =	9998·7	p =	0
H_2SO_4 +	400	H_2O	„ =	10099	„	1·34
„	200	„	„	10192	„	2·65
„	100	„	„	10372	„	5·16
„	50	„	„	10716	„	9·82
„	25	„	„	11336	„	17·88

[52] For example, if it be given that at 19° the sp. gr. of pure sulphuric acid = 18330, then at 20° it = 18330 − (20 − 19)10·13 = 18320.

[53] The historical and experimental details concerning the sp. gr. of solutions of sulphuric acid are given in Chapter III. of my work, *The Investigation of Aqueous Solutions according to their Specific Gravities* (1887).

$H_2SO_4 + 12\frac{1}{2}\ H_2O$	$s =$	12345	$p =$	30·34
„ 10 „ „		12760	„	35·25
„ 5 „ „		14306	„	52·13
„ $3\frac{1}{3}$ „ „		15370	„	62·02
„ $2\frac{1}{2}$ „ „		16102	„	68·53
„ 2 „ „		16655	„	73·13
„ 1 „ „		17943	„	84·48
„ $\frac{1}{2}$ „ „		18435	„	91·59
H_2SO_4		18528	„	100
$SO_3 + 4H_2SO_4$		19075	„	103·8
$2SO_3 + 3H_2SO_4$		19793	„	107·9.

Where p is weight per cent. of H_2SO_4.

The investigation of the increase of the specific gravity with a rise of the percentage amount of the normal hydrate H_2SO_4—that is, the magnitudes of ds/dp (the quotient of s by p)—shows that in this respect also the definite hydrates H_2SO_4 and $H_2SO_4H_2O$ clearly stand out among the solutions. The variations of these increments are given on the accompanying diagram, where the percentage amounts of H_2SO_4 in the solutions are laid out along the axes of abscissæ, and the magnitudes of these increments are laid along the axes of the ordinates. It is seen that these magnitudes lie in straight lines, proceeding from one definite hydrate to another, where they undergo a rupture and change their direction. This is most clearly seen in the normal hydrate H_2SO_4 ($p=100$ p.c.). From H_2SO_4,H_2O to H_2SO_4 ds/dp is expressed by the straight line $729-7{\cdot}49p$, and therefore when $p=100$, the increment of the specific gravity ds/dp is a negative quantity $= -20$; this signifies that in approaching to the hydrate H_2SO_4, the specific gravity does not rise, but falls, with the increase of the amounts of H_2SO_4. And in reality Kohlrausch, Schertel, and others found that the specific gravity of the normal acid is less than that of its first mixtures with water, and that the maximum specific gravity (when $ds/dp=0$) corresponds not with H_2SO_4—that is, not to $p=100$—but nearly with $p=97\frac{1}{2}$ p.c. And thus, according as the aqueous acid by the addition of sulphuric anhydride approaches from $97\frac{1}{2}$ p.c. to 100 p.c., or H_2SO_4, the specific gravity falls, $ds/dp = -20$. But directly the addition of sulphuric anhydride is in excess of that needed to form the hydrate H_2SO_4, and fuming sulphuric acid begins to be formed, the specific gravity begins to rise—thus, then $s=18528+129\ (p-100)+3{\cdot}9\ (p-100)^2$,[54]

[54] In order to preserve the same form of expression for the composition of fuming sulphuric acid as for the weaker solutions, I take p as that quantity of normal acid H_2SO_4 which may be obtained from 100 parts by weight of a given solution. If $p=$

therefore ds/dp then $=129+7{\cdot}8\,(p-100)$, consequently when $p=100$ the magnitude ds/dp is no longer negative but positive, and $=129$. That is, at the point H_2SO_4 there is a rupture in the continuity of ds/dp

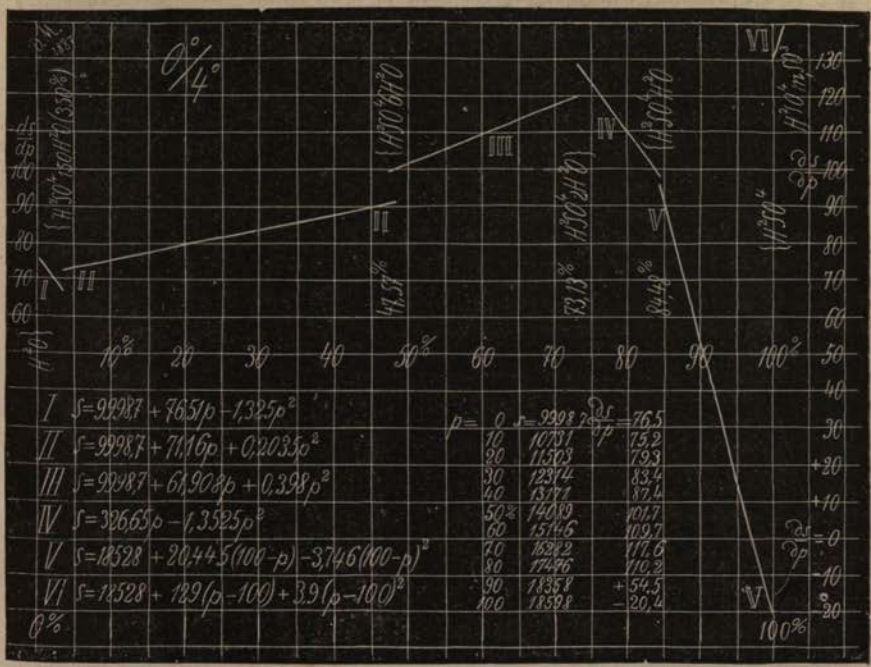


FIG. 89.—Diagram showing the variation of the factor (ds/dp) of the specific gravity of solutions of sulphuric acid. The percentage quantities of the acid, H_2SO_4, are laid out on the axes of abscissæ. The ordinates are the factors or rises in sp. gr. (water at 4 = 10000) with the increase in the quantity of H_2SO_4.

from −20 to +129, as is seen from the diagram, where VV depict ds/dp from H_2SO_4,H_2O to H_2SO_4 and VI depicts ds/dp from H_2SO_4 in the direction of fuming sulphuric acid.

In a like manner it may be shown that the increment or quotient ds/dp attains a maximum value (among all solutions of sulphuric acid in water) at the hydrate $H_2SO_4,2H_2O$, which corresponds with the greatest contraction and rise of temperature in the admixture of sulphuric acid with water. And as this hydrate has the composition $S(OH)_6=H_2SO_4,2H_2O$, which corresponds with many salts—for in-

95 p.c., it signifies that out of 100 grams of this acid 95 grams of the normal acid H_2SO_4 may be obtained (by the removal of water); if $p=110$ p.c. it means that from 100 grams of the given acid we can obtain (by adding water) 110 grams of the acid H_2SO_4. It is obvious that for fuming acids p is greater than 100. For sulphuric anhydride the value of p is 122·5.

stance, with $CaSO_4,2H_2O$—therefore, although it is not known in a solid form like $H_2SO_5H_2O=SO(OH)_4$ and $H_2SO_4=SO_2(OH)_2$, still it must be recognised as a definite compound of water and sulphuric acid.[55]

In practice, where sulphuric acid is used in immense quantities it is very important to be able to accurately and rapidly determine the amount of normal hydrate in aqueous solutions. For this purpose recourse is generally had to the determination of the specific gravity, and therefore we give below a table of the specific gravities of solutions of sulphuric acid, for four temperatures t, taking the sp. gr. of water at $4°=1000$,[56]

	0°	10°	20°	30°
0 p. c.	0·9999	0·9997	0·9983	0·9958
10	1·073	1·070	1·066	1·061
20	1·150	1·145	1·139	1·133
30	1·232	1·224	1·217	1·210
40	1·317	1·309	1·301	1·294
50	1·409	1·401	1·393	1·385
60	1·515	1·506	1·497	1·488
70	1·629	1·619	1·609	1·599
80	1·748	1·737	1·726	1·716
90	1·836	1·825	1·814	1·804
100	1·853	1·842	1·832	1·822

The great affinity of sulphuric acid for water is also seen from the fact that when the strong acid acts on the majority of *organic*

[55] Although not so clearly proved, still, judging from the specific gravities, we should recognise another hydrate, $H_2SO_4,6H_2O$, and one more very highly hydrated hydrate, $H_2SO_4,150H_2O$, at which point the direction of ds/dp changes (as is seen in the diagram), but whose composition cannot yet be accurately determined with the sum of the data now at our disposal. The researches (see Note 53) made by me in this direction have since found indirect confirmation in the careful observations on solutions of ferric chloride and zinc chloride (Chapter XVI. Note 4) carried on by Cheltzoff, which show that for these salts dt/dp exhibits nearly the same changes as sulphuric acid. Besides which, H. Crompton (1888), in his researches on the electrical conductivity of solutions of sulphuric acid, and Tammann, in his observations on their vapour tension, found a correlation with the hydrates indicated, as above, by the investigation of their specific gravities. This subject, which has so recently entered into the literature of chemistry, and which is connected with the theory of the dissociation of the hydrates occurring (Chapter I.) in solutions, will probably be elucidated by further work, and requires fresh special research.

[56] Besides which, the following are the sp. gr. about 100 p.c.:—

	0°	10°	20°	30°
96 p.c.	1·855	1·844	1·834	1·824
98 „	1·855	1·845	1·834	1·824
100 „	1·853	1·842	1·832	1·822
102 „	1·880	1·869	1·859	1·848
104 „	1·911	1·899	1·888	1·878

substances (especially when heated) it very frequently *takes up the elements of water* occurring in them. Thus strong sulphuric acid acting on alcohol, C_2H_6O, takes up the elements of water from it, and converts it into olefiant gas, C_2H_4. It acts in a similar manner on wood and other vegetable tissues, which it chars. If a piece of wood be immersed in strong sulphuric acid it turns black. This is owing to the fact that the wood contains carbohydrates which give up hydrogen and oxygen as water to the sulphuric acid, leaving charcoal, or a black mass very rich in it, behind. For example, cellulose, $C_6H_{10}O_5$, acts in this manner. Hence it is said, that sulphuric acid *chars* organic matter.[57]

The second most important peculiarity of sulphuric acid is its distinct and very *energetic acid properties*, which we have already had frequent occasion to notice, and therefore we will now only consider a few of their aspects. First of all we must remember that, with calcium, strontium, and especially with barium and lead, sulphuric acid forms very slightly soluble salts, whilst with the majority of other metals it gives more easily soluble salts, which in the majority of cases are able, like sulphuric acid itself, to combine with water to form crystallo-hydrates. Normal sulphuric acid, containing two atoms of hydrogen in its molecule, is able already for this reason alone to form two classes of salts, *normal* and *acid*, which it does with great facility *with the alkali metals*. The metals of the alkaline earths and the majority of other metals, if they do form acid sulphates, do so under exceptional conditions (with an excess of strong sulphuric acid), and these salts when formed are decomposable by water—that is, although having a certain degree of physical stability they have no chemical stability. Besides the acid salts $RHSO_4$, sulphuric acid also gives other forms of acid salts. An entire series of salts having the composition $RHSO_4,H_2SO_4$, or for bivalent metals $RSO_4,3H_2SO_4$,[58] have been prepared. Such

[57] If sulphuric acid be kept in an open vessel, the organic matter of the dust held in the atmosphere falls into it and blackens the acid. The same thing happens if sulphuric acid is kept in a bottle closed by a cork, because the cork becomes charred, and the acid turns black. However, the chemical properties of the acid undergo a very slight change when it turns black, so that it is still fit for many purposes. Sulphuric acid which is considerably diluted with water does not produce the above effects, which clearly shows their dependence on the affinity of the sulphuric acid for water. It is evident from the preceding that strong sulphuric acid will act as a powerful poison; whilst, on the other hand, when very dilute it is even employed as a fertiliser, and it is sometimes poured directly over fields destined for vegetation, and sometimes plants themselves are washed with it. If taken internally by animals in a very dilute solution it has very little action, although the strong acid is a very powerful poison, just as acetic acid in a very strong solution is poisonous, and a dilute solution forms the vinegar used for consumption.

[58] Weber (1884) obtained a series of salts $R_2O,8SO_3$ for K, Rb, Cs, and Tl.

salts have been obtained for potassium, sodium, nickel, calcium, silver, magnesium, manganese. They are prepared by dissolving the sulphates in an excess of sulphuric acid, and heating the solution until the excess of sulphuric acid is driven off; on cooling, the mass solidifies into a crystalline salt. Besides which, Rose obtained a salt having the composition $Na_2SO_4,NaHSO_4$, and if $HNaSO_4$ be heated it easily forms a salt $Na_2S_2O_7=Na_2SO_4,SO_3$; hence it is clear that suphuric anhydride combines with various proportions of bases, just as it combines with various proportions of water.

We already know that sulphuric acid displaces the acid from the salts of nitric, carbonic, and many other volatile acids. Berthollet's laws, as we have seen (Chapter X.), explain this fact, and show that sulphuric acid does not *displace* the above *acids*, because it has a greater affinity for bases, but only because of its small volatility; and, indeed, in an aqueous solution sulphuric acid displaces the much less soluble boric acid from its compounds—for instance, from borax, and it also displaces silica from its compounds with bases; but both boric anhydride and silica, when fused with sulphates, decompose them, displacing sulphuric anhydride, SO_3, because they are less volatile than sulphuric anhydride and sulphuric acid itself.

The reactions of sulphuric acid *with respect to organic substances* are generally determined by its acid character, when the direct extraction of water, or oxidation at the expense of the oxygen of the sulphuric acid,[59] or disintegration does not take place. So, for example, with sulphuric acid the majority of the saturated hydrocarbons, C_nH_{2m}, form a special class of *sulphonic acids*, $C_nH_{2m-1}(HSO_3)$; for example, benzene, C_6H_6, forms benzenesulphonic acid, $C_6H_5{\cdot}SO_3H$, water being separated, for the formation of which oxygen is taken up from the sulphuric acid, because the product contains less oxygen than the sulphuric acid. It is evident from these acids that the hydrogen in organic compounds is replaceable by the group SO_3H, just as it may be replaced by the radicles Cl, NO_2, CO_2H, and others. As the radicle

[59] For example, the action of hot sulphuric acid on nitrogenous compounds, as applied in Kjeldahl's method for the estimation of nitrogen (Vol. I. p. 246). It is obvious that when sulphuric acid acts as an oxidising agent, it forms sulphurous anhydride.

The action of sulphuric acid on the alcohols is exactly similar to its action on alkalis, because the alcohols, like alkalis, react on acids; a molecule of alcohol with a molecule of sulphuric acid separates water and forms an *acid* ethereal salt—that is, there is produced an ethereal compound corresponding with acid salts. Thus, for example, the action of sulphuric acid, H_2SO_4, on common alcohol, C_2H_5OH, gives water and sulphovinic acid, $C_2H_5HSO_4$—that is, sulphuric acid in which one atom of hydrogen is replaced by the radicle C_2H_5 of ethyl alcohol, $SO_2(OH)(OC_2H_5)$, or, which is one and the same thing, the hydrogen in alcohol is replaced by the radicle (sulphoxyl) of sulphuric acid, $C_2H_5O{\cdot}SO_2(OH)$.

of sulphuric acid or *sulphoxyl*, SO_2OH or SHO_3, contains, like carboxyl (Vol. I. p. 383), one hydrogen (hydroxyl) of sulphuric acid, therefore the resultant substances are acids whose basicity is equal to the number of hydrogens replaced by sulphoxyl. And as sulphoxyl takes the place of hydrogen, and itself contains hydrogen, therefore the sulpho-acids are equal to a hydrocarbon $+SO_3$, just as every organic (carboxylic) acid is equal to a hydrocarbon $+CO_2$. Moreover, here this relation corresponds with the direct reaction, because many sulphonic acids are obtained by the direct combination of sulphuric anhydride: $C_6H_5(SO_3H) = C_6H_6 + SO_3$. The sulphonic acids give soluble barium salts, and are therefore easily distinguished from sulphuric acid. They are soluble in water, are not volatile, and when distilled give sulphurous anhydride (whilst the hydroxyl previously in combination with the sulphurous anhydride remains in the hydrocarbon group; thus phenol, $C_6H_5{\cdot}OH$, is obtained from benzenesulphonic acid), and they are very energetic, because the hydrogen acting in them is of the same nature as in sulphuric acid itself.[60]

Sulphuric acid, as containing a large proportion of oxygen, is a substance which frequently acts as an oxidising agent: in which case it is *deoxidised, forming sulphurous anhydride* and water (or even, although more rarely, sulphuretted hydrogen and sulphur). Sulphuric acid acts in this manner on charcoal, copper, mercury, silver, organic and other substances, which are unable to evolve hydrogen from it directly, as we saw in describing sulphurous anhydride.

Although a higher form of oxide capable of giving salts, sulphuric

[60] We will mention the following difference between the sulphonic acids and the ethereal acid sulphates (Note 59): the former re-form sulphuric acid with difficulty and the latter easily. Thus sulphovinic acid when heated with an excess of water is reconverted into alcohol and sulphuric acid. This is explained in the following manner. Both these classes of acids are produced by the substitution of hydrogen by SO_3H, or the univalent radicle of sulphuric acid, but in the formation of ethereal acid sulphates the SO_3H replaces the hydrogen of the hydroxyl in the alcohol, whilst in the formation of the sulphonic acids the SO_3H replaces the hydrogen of a hydrocarbon. This difference clearly evinces itself in the existence of two acids of the composition $SO_4C_2H_6$. The one, mentioned above, is alcohol, $C_2H_5{\cdot}OH$, in which the hydrogen of the hydroxyl is replaced by sulphoxyl $= C_2H_5{\cdot}OSO_3H$, whilst the other is alcohol, in which one atom of the hydrogen in ethyl, C_2H_5, is replaced by the sulphonic group—that is $= C_2H_4(SO_3H){\cdot}OH$. The latter is called isethionic acid. It is more stable than sulphovinic acid. The details as to these interesting compounds must be looked for in organic chemistry, but I think it necessary to note one of the general methods of formation of these acids. The sulphites of the alkalis—for example, K_2SO_3—when heated with the halogen products of metalepsis, give a halogen salt and a salt of a sulphonic acid. Thus methyl iodide, CH_3I, corresponds with marsh gas, CH_4, and at 100° with a solution of potassium sulphite, K_2SO_3, it gives potassium iodide, KI, and potassium methylsulphonate, CH_3SO_3K—that is, a salt of the sulphonic acid. This shows that the sulphonic acid may be referred to sulphurous acid, because there is a resemblance between sulphuric and sulphurous acid, which clearly evinces itself here in the formation of one product from them both.

anhydride is capable of further oxidation, and forms a kind of peroxide, just as hydrogen gives hydrogen peroxide, in addition to water, or as sodium and potassium, besides the oxides Na_2O and K_2O, give their peroxides, compounds which are in a chemical sense unstable, powerfully oxidising, and which do not directly enter into saline combinations. If the oxides of potassium, barium, &c., be likened to water, then their peroxides must naturally be likened to hydrogen peroxide,[61] not only because the oxygen contained in them is very mobile and easily liberated, and because their reactions are similar, but also because they can be mutually transformed into each other, and because, although they do not give true salts, they are able to form mutual compounds and hydrates, as is seen from Schöne's researches, who obtained a compound of barium peroxide with hydrogen peroxide.[62] And this is the character of *sulphuric peroxide*, S_2O_7, discovered in 1878 by Berthelot, and called by him *persulphuric acid*, although it does not form salts, nor exhibit any properties that can justify its being termed an acid;[63] thus it decomposes spontaneously, and is

[61] The reaction $BaO + O$ develops 12000 heat units, whilst the reaction $H_2O + O$ absorbs −21000 heat units.

[62] If barium peroxide be dissolved in hydrochloric (or acetic) acid, or if a solution of hydrogen peroxide be diluted with a solution of barium hydroxide, a pure hydrate is precipitated having the composition $BaO_2,8H_2O$ (sometimes the composition is taken as $BaO_2,6H_2O$). This fact was already known to Thenard. Schöne showed that if hydrogen peroxide be in excess, a crystalline compound of both peroxides, BaO_2,H_2O_2, is precipitated. Schöne also obtained small well-formed crystals of the same composition by adding a solution of ammonia to an acid solution of barium peroxide (containing a barium salt and hydrogen peroxide). Thus barium peroxide combines with both water and hydrogen peroxide. This is a very important fact for the comprehension of the composition of other peroxides, which has recently occupied the attention of many chemists.

[63] There is only one circumstance which might cause the oxide S_2O_7 to be named as it was by Berthelot, but this circumstance is purely external and conditional, and depends on the fact that the dioxides MnO_2 and PbO_2 are frequently called peroxides, although they are of a different nature from the true peroxides, H_2O_2, BaO_2, Na_2O_2, &c. Manganese and its analogues, which give bases and acids, form peroxides from basic oxides *plus* oxygen, and the peroxides *plus* oxygen give the acids; and among them is MnO_3 the analogue of SO_3, and Mn_2O_7 the analogue in composition of S_2O_7. But it is evident that the properties of the peroxides are independent, and MnO_2 has as little resemblance to the peroxides of hydrogen, sodium, and barium as it has to the oxides PtO_2, SO_2, SiO_2, and even PbO_2, although here the oxides are formed on the same type. In the first place, those true peroxides, among which S_2O_7 must be reckoned, present a higher type of oxide than the salt-forming oxide (and in the case of MnO_2 there are still higher acid oxides, MnO_3 and Mn_2O_7), and in the second place they contain oxygen, which is as easily liberated in reactions as in hydrogen peroxide.

In order to clearly demonstrate the possibility of a peroxide form for acids, it should be mentioned that Brodie long ago obtained the so-called *acetic peroxide* $(C_2H_2O)_2O_2$, by the action of barium peroxide on acetic anhydride $(C_2H_3O)_2O$. Its corresponding hydrate is also known. This shows that true peroxides and their hydrates, with reactions similar to those of hydrogen peroxide, may be possible for acids, as we find to be the case with acetic peroxide and its hydrate. And such, in my opinion, is the

formed from $2SO_3+O$ with the absorption of heat (-27 thousand heat units), like ozone from O_2+O (-29 thousand units of heat), or hydrogen peroxide H_2O+O (-21 thousand heat units). It gives a compound with hydrogen peroxide like that formed by barium peroxide; it is formed from strong sulphuric acid and hydrogen peroxide, exactly like calcium peroxide; it is even decomposed by platinum, and presents all the characters of the true peroxides.

The hydrate of sulphuric peroxide, $S_2O_7,H_2O=S_2H_2O_8$, is obtained more simply by mixing strong sulphuric acid (not weaker than $H_2SO_4,2H_2O$) directly with hydrogen peroxide, or by the action of a galvanic current on sulphuric acid mixed with a certain amount of water, and cooled, the electrodes being platinum wires, when it naturally appears at the positive pole.[61] When an acid of the strength $H_2SO_4,6H_2O$ is taken, then at first the hydrate of the sulphuric peroxide, S_2O_7,H_2O, only is formed; but when the concentration about the positive pole reaches $H_2SO_4,3H_2O$, then a mixture of hydrogen peroxide and the hydrate of sulphuric peroxide begins to be formed. A

relation of S_2O_7 and its compounds with water and hydrogen peroxide to sulphuric acid, and therefore I call S_2O_7 the sulphur peroxide or the sulphuryl peroxide. It is evident from the above that similar peroxides may be expected for other acids also. A similar higher oxide has long been known for chromium, and Berthelot obtained a like compound for nitric acid; but these have been far less studied than S_2O_7, which Berthelot discovered and investigated with a certain amount of detail.

Anhydrous *sulphuric peroxide*, S_2O_7, is obtained by the prolonged (8 to 10 hours) action of a silent discharge of considerable intensity on a mixture of oxygen and sulphurous anhydride; the vapour of sulphuric peroxide, S_2O_7, condenses as liquid drops, or after being cooled to 0° in the form of long prismatic crystals, resembling those of sulphuric anhydride. The anhydrous compound S_2O_7 (and also the hydrous) cannot be preserved long, as it splits up into oxygen and sulphuric anhydride. Direct experiment shows that a mixture of equal volumes of sulphurous anhydride and oxygen leaves a residue of a quarter of the oxygen taken, or half of the whole volume, which indicates the formula S_2O_7. This substance is soluble in water, and it then gives a hydrate, probably having the composition $S_2O_7,H_2O=2SHO_4$. This solution oxidises the salts SnX_2, potassium iodide, and others, which renders it possible to prove that the solution actually contains one atom of oxygen capable of effecting oxidation to two molecules of sulphuric anhydride.

[61] Many other peroxides of various elements may be obtained by a similar method of double decomposition or by the action of a galvanic current (when the higher oxygen compound is formed at the anode). Thus Spring (1889), by acting at the ordinary temperature with an excess of pure hydrated barium peroxide (precipitated from a solution of hydrogen peroxide by the addition of barium hydroxide) on a solution of stannous chloride (saturated and containing hydrochloric acid), obtained a cloudy solution, which after dialysis (lasting three months, with the daily renewal of the external water) and evaporation left a white mass having the composition $H_2Sn_2O_7$. Spring regarded this substance as a hyperstannic acid, although he did not obtain any corresponding salts. It appears to me possible to admit that the substance is a compound of hydrogen peroxide with *tin peroxide*, Sn_2O_5, because $Sn_2H_2O_7=H_2O_2+Sn_2O_5$, although it is also possible to admit that the peroxide forms of tin are Sn_2O_5 and SnO_3, and if the substance obtained contains SnO_3, then $Sn_2O_7H_2$ is $H_2O,2SnO_3$.

state of equilibrium is ultimately arrived at between the amount of these substances which corresponds with the proportion $S_2O_7 : 2H_2O_2$, which, as it were, answers to a hydrate $S_2O_9,2H_2O$. But its existence cannot be recognised, because the sulphuric peroxide can be easily distinguished from the hydrogen peroxide in the solution, owing to the fact that the former does not act on an acid solution of potassium permanganate, whilst the hydrogen peroxide evolves both its own oxygen and that of the permanganic acid and converts it into manganous oxide; this enables the relative amounts of S_2O_7 and H_2O_2 to be determined. Their common property of liberating iodine from an acid solution of potassium iodide enables the sum of active oxygen in them both to be determined. Dilute solutions of sulphuric peroxide can be kept better than more concentrated solutions, and the latter may be obtained containing as much as 123 grams of the peroxide to a litre. It is a very instructive fact that hydrogen peroxide is always formed when strong solutions of sulphuric peroxide break up on keeping. So that the bond between both peroxides is established both by analysis and synthesis: hydrogen peroxide is able to give sulphuric peroxide, and the latter to give hydrogen peroxide. A mixture of sulphuric peroxide with sulphuric acid or water is immediately decomposed, with the evolution of oxygen, either when heated or under the action of spongy platinum. The same thing takes place with a solution of baryta, only not so rapidly, so that the solution may be filtered. Mercury, ferrous oxide, and the stannous salts, are oxidised by sulphuric peroxide. These are all distinct signs of true peroxides.

In order to see the relations of sulphuric peroxide, we must first remark that hydrogen peroxide is considered, in the sense of the law of substitutions, as water, H(OH), in which H is replaced by (OH): $OHOH=H_2O_2$. The relation of $H_2S_2O_8$ or H_2O,S_2O_7 to H_2SO_4 is exactly similar. Indeed, the radicle of sulphuric acid, equivalent to hydrogen, is HSO_4;[65] it corresponds with the (OH) of water, and therefore sulphuric acid, $H(SHO_4)$, gives $(SHO_4)_2$ or $S_2H_2O_8$, in exactly the same manner as water gives $(HO)_2$—*i.e.* H_2O_2.[66]

[65] Or one of those supposed ions which appear at the positive pole in the decomposition of sulphuric acid by the action of a galvanic current.

[66] If this be true one would expect the following peroxide hydrates: for phosphoric acid, $(H_2PO_4)_2 = H_4P_2O_8 = 2H_2O + 2PO_3$; for carbonic acid, $(HCO_3)_2 = H_2C_2O_6 = H_2O + C_2O_5$; and for lead the true peroxide will be also Pb_2O_5, &c. Judging from the example of barium peroxide (Note 62), these peroxide forms will probably combine together. It seems to me that the compounds obtained by Fairley for uranium are very instructive as elucidating the peroxides. In the action of hydrogen peroxide in an acid solution on uranium oxide, UO_3, there is formed a uranium peroxide, $UO_4,4H_2O$ (U = 240), but hydrogen peroxide acts on uranium oxide in the presence of caustic soda; then on the addition of alcohol a crystalline compound containing $Na_4UO_8,4H_2O$ is precipitated,

The largest proportion *of sulphuric acid is used* for reacting on sodium chloride in the manufacture of sodium carbonate; for the manufacture of the volatile acids, like nitric, hydrochloric, &c., from their corresponding salts; for the preparation of ammonium sulphate, alums, vitriols (copper and iron), and other salts of sulphuric acid; in the treatment of bone-ash for the preparation of phosphorus, and for the solution of metals—for example, of silver in its separation from gold—for cleaning metals from rust, &c. A large amount of oil of vitriol is also used in treatment of organic substances; it is used for the extraction of stearin, or stearic acid, from tallow, for refining petroleum and various vegetable oils, for purifying madders, for the solution of indigo and other colouring matters, for the conversion of paper into vegetable parchment, for the preparation of ether from alcohol, for the preparation of various artificial scents from fusel oil, for the preparation of vegetable acids, such as oxalic, tartaric, citric, for the conversion of non-fermentable starchy substances into fermentable glucose, and in a number of other processes. It would be difficult to find another artificially-prepared substance which is so frequently applied in the arts as sulphuric acid. Where there are not works for its manufacture, the rational production of many other substances of great technical importance is impossible. In those localities which have arrived at a high technical activity the amount of sulphuric acid consumed is proportionally large; sulphuric acid, sodium carbonate, and lime are the most important of the artificially-prepared agents employed at technical works.

Besides the normal acids of sulphur, H_2SO_3, H_2SO_3S, and H_2SO_4, corresponding with sulphuretted hydrogen, H_2S, in the same way that the oxy-acids of chlorine correspond with hydrochloric acid, HCl, there exists a particular series of acids which are termed *thionic acids*. Their general composition is $S_nH_2O_6$, where n varies from 2 to 5. If $n=2$, the acid is called dithionic acid. The others are distinguished as trithionic, tetrathionic, and pentathionic acids. Their composition, existence, and reactions are very easily understood if they be referred to the class of the sulphonic acids—that is, if their relation to sulphuric acid be expressed in just the same manner as the relation of the organic acids to carbonic acid. The organic acids, as we saw (Chapter IX.), proceed from the hydrocarbons by the substitution of their hydrogen by carboxyl—that is, by the radicle of carbonic acid,

which is doubtless a compound of the peroxides of sodium, Na_2O_2, and uranium, UO_4. It is very possible that the first peroxide, $UO_4,4H_2O$, contains the elements of hydrogen peroxide and uranium peroxide, U_2O_7, or even $U(OH)_6,H_2O_2$, just as the peroxide form lately discovered by Spring for tin perhaps contains Sn_2O_5,H_2O_2.

$CH_2O_3 - HO = CHO_2$. The formation of the acids of sulphur may be represented in the same manner. Therefore to hydrogen there should correspond the acids $HSHO_3$, sulphurous, and $SHO_3 \cdot SHO_3 = S_2H_2O_6$, or dithionic; for SH_2 there should correspond the acids $SH(SHO_3) = H_2S_2O_3$ (thiosulphuric), and $S(SHO_3)_2 = H_2S_3O_6$ (trithionic); for S_2H_2 the acids $S_2H(SHO_3) = H_2S_3O_2$ (unknown), and $S_2(SHO_3)_2 = H_2S_4O_6$ (tetrathionic); for S_3H_2 the acids $S_3H(SHO_3)$ and $S_3(SHO_3)_2 = H_2S_5O_6$ (pentathionic). Iodine reacts directly with the hydrogen of sulphuretted hydrogen and combines with it, and it reacts still more clearly with the metals which have replaced this hydrogen. Thiosulphuric acid contains the radicle of sulphuretted hydrogen or hydrogen (united with sulphur) of the same nature as in sulphuretted hydrogen; so it is not, therefore, surprising that iodine reacts on sodium thiosulphate and forms sodium tetrathionate. So, thiosulphuric acid, $HS(SHO_3)$, when deprived of H, gives a radicle which immediately combines with another similar radicle, forming the tetrathionate $S_2(SO_2HO)_2$. With this view [67] of the structure of the thionic acids and salts, it is also clear how all the thionic acids, like thiosulphuric acid, easily give sulphur and sulphides, with the exception only of dithionic acid, $H_2S_2O_6$, which, judging from the above, stands apart from the series of the other thionic acids. Dithionic acid stands in the same relation to sulphuric acid as oxalic acid does to carbonic acid. Oxalic acid is dicarboxyl, $(CHO_2)_2 = C_2H_2O_4$, and so also dithionic acid is disulphoxyl, $(SHO_3)_2 = S_2H_2O_6$. Oxalic acid when ignited decomposes into carbonic anhydride and carbonic oxide, CO, and dithionic acid when heated decomposes into sulphuric anhydride and sulphurous anhydride, SO_2, and SO_2 stands in the same relation to SO_3 as CO to CO_2. This also explains the peculiarity of the calcium, barium, and lead, &c., salts of the thionic acids being easily soluble, although the corresponding salts of H_2SO_3, H_2SO_4, and H_2S dissolve with difficulty, because the former are similar to the salts of the sulphonic acids, which are also soluble in water. Thus the thionic acids are *disulphonic acids*, just as many dicarboxylic acids are known for carbon—for example, $CH_2(CO_2H)_2$, $C_6H_4(CO_2H_2)$.[68]

[67] This view was communicated by me in 1870 to the Russian Chemical Society (*Journal of the Russian Chemical Society*, 1870, p. 276).

[68] *Dithionic acid*, $H_2S_2O_6$, is distinguished among the thionic acids as containing the least proportion of sulphur. It is also called hyposulphuric acid, because its supposed anhydride, S_2O_5, contains more O than sulphurous oxide, SO_2 or S_2O_4, and less than sulphuric anhydride, SO_3 or S_2O_6. Dithionic acid, discovered by Gay-Lussac and Welter, is known as a hydrate and as salts, but not as anhydride. The method for preparing dithionic acid usually employed is by the action of finely-powdered manganese dioxide on a solution of sulphurous anhydride. On shaking, the smell of the latter disappears, and the manganese salt of the acid in question passes into solution;

Sulphur exhibits an acid character, not only in its compounds with hydrogen and oxygen, but also in those with other elements. The

$MnO_2 + 2SO_2 = MnS_2O_6$. If the temperature be raised, the dithionate splits up into sulphurous anhydride and manganese sulphate, $MnSO_4$. Generally owing to this a mixture of manganese sulphate and dithionate is obtained in the solution. They may be separated by mixing the solution of the manganese salts with a solution of barium hydroxide, when a precipitate of manganese hydroxide and barium sulphate is obtained. In this manner barium dithionate only is obtained in solution. This salt is purified by crystallisation, in which form it separates as $BaS_2O_6,2H_2O$; this is then dissolved in water, and decomposed with the requisite amount of sulphuric acid. Dithionic acid, $H_2S_2O_6$, then remains in solution. By concentrating the resultant solution under the receiver of an air-pump it is possible to obtain a liquid of sp. gr. 1·347, but it still contains water, and on further evaporation the acid decomposes into sulphuric acid and sulphurous anhydride: $H_2S_2O_6 = H_2SO_4 + SO_2$. The same decomposition takes place if the solution be slightly heated. Like all the thionic acids, dithionic acid is readily attacked by oxidising agents, and passes into sulphurous acid. No dithionate is able to withstand the action of heat, even when very slight, without giving off sulphurous anhydride: $K_2S_2O_6 = K_2SO_4 + SO_2$. The alkali dithionates have a neutral reaction (which indicates the energetic nature of the acid), are soluble in water, and in this respect present a certain resemblance to the salts of nitric acid. The latter circumstance probably depends on the analogy of the atomic composition of dithionic and nitric acids and of their salts. Thus their anhydrides are N_2O_5 and S_2O_5, their barium salts BaN_2O_6 and BaS_2O_6; but a difference must be recognised in the salts of the univalent metals KNO_3 and $K_2S_2O_6$, although the latter formula is divisible by two.

Langlois, about 1840, obtained a particular thionic acid by heating a strong solution of potassium acid sulphite with flowers of sulphur to about 60°, until the disappearance of the yellow coloration first produced by the solution of the sulphur. On cooling, a portion of the sulphur was precipitated, and there separated out crystals of a salt of *trithionic acid*, $K_2S_3O_6$ (partly mixed with potassium sulphate). Plessy afterwards showed that the action of sulphurous acid on a thiosulphate also gives sulphur and trithionic acid: $2K_2S_2O_3 + 3SO_2 = 2K_2S_3O_6 + S$. A mixture of potassium acid sulphite and thiosulphate also gives a trithionate. It is very possible that a reaction of the same kind occurs in the formation of trithionic acid by Langlois's method, because potassium sulphite and sulphur yield potassium thiosulphate. The potassium thiosulphate may also be replaced by potassium sulphide, and on passing sulphurous anhydride through the solution thiosulphate is first formed and then trithionate: $4KHSO_3 + K_2S + 4SO_2 = 3K_2S_3O_6 + 2H_2O$. The sodium salt is not formed under the same circumstances as the corresponding potassium salt. The sodium salt does not crystallise and is very unstable; the barium salt is, however, more stable. The barium and potassium salts are anhydrous, they give neutral solutions, and decompose when ignited, with the evolution of sulphur and sulphurous anhydride, a sulphate being left behind—for example, $K_2S_3O_6 = K_2SO_4 + SO_2 + S$. If a solution of the potassium salt be decomposed by means of hydrofluosilicic or chloric acid, the insoluble salts of these acids are precipitated, and trithionic acid is obtained in solution, which, however, very easily breaks up on concentration. The addition of salts of copper, mercury, silver, &c., to a solution of a trithionate, is followed, either immediately or after a certain time, by the formation of a black precipitate of the sulphides whose formation is due to the decomposition of the trithionic acid with the transference of its sulphur to the metal.

Tetrathionic acid, $H_2S_4O_6$, in contradistinction to the preceding acids, is much more stable in the free state than in the form of salts. In the latter form it is easily converted into trithionate, with liberation of sulphur. Sodium tetrathionate was obtained by Fordos and Gélis, by the action of iodine on a solution of sodium thiosulphate. The reaction essentially consists in the iodine taking up half the sodium of the thiosulphate, inasmuch as the latter contains $Na_2S_2O_3$, whilst the tetrathionate contains

compound of sulphur and carbon has been particularly well investigated. It presents a great analogy to carbonic anhydride, both in its elementary composition and chemical character. This substance is the so-called carbon bisulphide, CS_2, and corresponds with CO_2.

NaS_2O_3 or $Na_2S_4O_6$, so that the reaction is as follows: $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$. It is evident that tetrathionic acid stands to thiosulphuric acid in exactly the same relation as dithionic acid does to sulphurous acid; for the same amount of the other elements in dithionate KSO_3, and tetrathionate KS_2O_3, there is half as much metal as in sulphite, K_2SO_3, and thiosulphate, $K_2S_2O_3$. If in the above reaction the sodium thiosulphate is replaced by the lead salt PbS_2O_3, the sparingly-soluble lead iodide PbI_2 and the soluble salt PbS_4O_6 are obtained. And the lead salt easily gives tetrathionic acid itself; for this purpose a solution of the salt is mixed with sulphuric acid until it ceases to give a precipitate of lead sulphate: $PbS_4O_6 + H_2SO_4 = PbSO_4 + H_2S_4O_6$. The lead salt may also be decomposed by sulphuretted hydrogen, but in this case a portion of the acid is decomposed, and evolves sulphurous anhydride. The solution of tetrathionic acid thus obtained may be evaporated directly over a water bath, and afterwards in a vacuum, when it gives a colourless liquid, which has no smell and an acid reaction. When dilute it may be heated to its boiling-point, but in a concentrated form it decomposes into sulphuric acid, sulphurous anhydride, and sulphur: $H_2S_4O_6 = H_2SO_4 + SO_2 + S_2$.

Pentathionic acid, $H_2S_5O_6$, also belongs to this series of acids. But little is known concerning it, either as hydrate or in salts. It is formed, together with tetrathionic acid, by the direct action of sulphurous acid on sulphuretted hydrogen in an aqueous solution; a large proportion of sulphur being precipitated at the same time: $5SO_2 + 5H_2S = H_2S_5O_6 + 5S + 4H_2O$.

If, as was shown above, the thionic acids are disulphonic acids, then they may be obtained, like other sulphonic acids, by means of potassium sulphite and sulphur chloride. Thus Spring demonstrated the formation of potassium trithionate by the action of sulphur dichloride on a strong solution of potassium sulphite: $2KSO_3K + SCl_2 = S(SO_3K)_2 + 2KCl$. If sulphur chloride be taken, then sulphur is also precipitated. The same trithionate is formed by heating a solution of double thiosulphates, for example, of $AgKS_2O_3$. Two molecules of the salts then form silver sulphide and potassium trithionate. If the thiosulphate be the potassium silver salt $SO_3K(AgS)$, then the structure of the trithionate must necessarily be $(SO_3K)_2S$. Previous to Spring's researches the action of iodine on sodium thiosulphate was an isolated accidentally discovered reaction; he, however, showed its general significance by testing the action of iodine on mixtures of different sulphur compounds. Thus with iodine, I_2, the mixture $Na_2S + Na_2SO_3$ forms $2NaI + Na_2S_2O_3$, whilst the mixture $Na_2S_2O_3 + Na_2SO_3 + I_2$ gives $2NaI + Na_2S_3O_6$—that is, trithionic acid stands in the same relation to thiosulphuric acid as the latter does to sulphuretted hydrogen. And this is the same as our mode of representation: by replacing one hydrogen in H_2S by sulphuryl we obtain thiosulphuric acid, $HSO_3{\cdot}HS$, and by replacing a second hydrogen in the latter again by sulphuryl we obtain trithionic acid, $(HSO_3)_2S$. Furthermore, Spring showed that the action of sodium amalgam on the thionic acids causes reverse reactions to those above indicated for iodine. Thus sodium thiosulphate with Na_2 gives $Na_2S + Na_2SO_3$, and Spring showed that the sodium here is not a simple element taking up sulphur, but that it itself enters into double decomposition, replacing sulphur; for he took a potassium salt and acted on it with sodium: $K_2S_2O_3 + Na_2 = NaKS + NaKSO_3$, or, for sake of clearness, we may write it thus: $KSO_3(SK) + NaNa = KSO_3Na + (SK)Na$. In a similar way sodium dithionate with sodium gives sodium sulphite: $(NaSO_3)_2 + Na_2 = 2NaSO_3Na$; sodium trithionate forms $NaSO_3Na$ and $NaSO_3{\cdot}SNa$, and tetrathionate forms sodium thiosulphate, $(NaSO_3)S_2(NaSO_3) + Na_2 = 2(NaSO_3)(NaS)$.

In all the oxidised compounds of sulphur we may note the presence of the elements

The first endeavours to obtain a compound of sulphur with carbon were unsuccessful, for although sulphur does combine directly with carbon, yet the successful formation of this compound requires distinctly definite conditions. If sulphur is mixed with charcoal and heated, it is completely driven off from the latter, and there is not obtained the smallest trace of carbon bisulphide. The formation of this compound requires that the charcoal should be first heated to a red heat, but not above, and then either the vapour of sulphur passed over it or lumps of sulphur thrown on to the red-hot charcoal, but in small quantities, so as not to lower the temperature of the charcoal. If the charcoal be heated to a white heat, the amount of carbon bisulphide formed is less. This depends, in the first place, on the carbon bisulphide dissociating at a high temperature.[69] In the second place, Favre and Silberman

of sulphurous anhydride, SO_2, the only product of the combustion of sulphur, and in this sense the conpounds of sulphur containing one SO_2 are—

$SO_2{}^{H}_{HO}$	$SO_2{}^{HO}_{HO}$	$SO_2{}^{C_6H_5}_{HO}$	$SO_2{}^{HS}_{HO}$
Sulphurous acid	Sulphuric acid	Benzene sulphonic acid	Thiosulphuric acid

while, according to this mode of representation, the thionic acids are—

$SO_2{}^{HO}_{SO_2{}^{HO}}$	$SO_2{}^{HO}_{SO_2{}^{S\ HO}}$	$SO_2{}^{HO}_{SO_2{}^{S_2\ HO}}$	$SO_2{}^{HO}_{SO_2{}^{S_3\ HO}}$
Dithionic	Trithionic	Tetrathionic	Pentathionic

Hence it is evident that SO_2 has (whilst CO_2 has not) the faculty for combination, and aims at forming SO_2X_2. These X_2 can $=O$, and one involuntarily asks oneself if the O_2 which occurs in SO_2 is not of the same nature as this oxygen, which assimilates itself to SO_2—that is, whether SO_2 does not correspond with the more general type SX_4, and its compounds with the type SX_6? To this we may answer 'Yes' and 'No'—'Yes' in the general sense which proceeds from the investigation of the majority of compounds, especially metals, where RO corresponds with RCl_2, RX; 'No' in the sense that sulphur does not give either SH_4, SH_6, nor SCl_6, and therefore the stages SX_4 and SX_6 are only observable in the oxygen compounds. In the sense of the type SX_6 one would expect a hydrate, $S(HO)_6$, although not SCl_6. And we must recognise this hydrate from a study of the compounds of sulphuric acid with water.

[69] Even light decomposes carbon bisulphide, but not to the extent of separating carbon; under the action of the sun's rays it is decomposed into sulphur and a solid substance which is considered to be carbon monosulphide; it is of a red colour, and its sp. gr. is 1·66. Thorpe (1889) observed a complete decomposition of carbon bisulphide under the action of a liquid alloy of potassium and sodium; it is accompanied by an explosion and the deposition of carbon and sulphur. A like complete decomposition of carbon bisulphide is also accomplished by the action of mercury fulminate (Chapter XVI. Note 26), and is due to the fact that *at the ordinary temperature* (at which carbon bisulphide is not produced) *the decomposition* of carbon bisulphide takes place with the development of heat—that is, it presents an exothermal reaction, like the decomposition of all explosives. It is very possible that at a higher temperature, when carbon bisulphide is formed, the *combination* of carbon with sulphur is also an exothermal reaction—that is,

showed that in the combustion of one gram of carbon bisulphide (the products will be CO_2+2SO_2) 3400 heat units are evolved—that is, the combustion of a molecular quantity of carbon bisulphide evolves 258400 heat units (according to Berthelot, 246000). From a molecule of carbon bisulphide we may obtain 12 parts of carbon, whose combustion evolves 96000 heat units and 64 parts by weight of sulphur, evolving by combustion (into SO_2) 140800 heat units. Hence we see that the component elements evolve less heat (237000 heat units) than carbon bisulphide—that is, that heat should be evolved (at the ordinary temperature) and not absorbed in its decomposition, and therefore that the formation of carbon bisulphide from charcoal and sulphur is in all probability accompanied by an absorption of heat.[70] Hence it is not surprising that it, like other compounds produced with an absorption of heat (ozone, nitrous oxide, hydrogen peroxide, &c.), is unstable, easily converted into the original substances from which it may be obtained. And, indeed, if the vapour of carbon bisulphide be passed through a red-hot tube, it is decomposed—that is, it dissociates—into sulphur and carbon. And this takes place at the temperature at which this substance is formed, just as water decomposes into hydrogen and oxygen at the temperature of its formation. In this absorption of heat in the formation of carbon bisulphide is explained the facility with which it suffers reactions of decomposition, which we shall see in the sequel, and its main difference from the closely analogous carbonic anhydride.

In the laboratory carbon bisulphide is prepared as follows. A porcelain tube is luted into a furnace in an inclined position, the upper extremity of the tube being closed with a cork, and the lower end connected with a condenser. Charcoal is then laid in the tube and

heat is developed. If this be the case, then carbon bisulphide would present a most instructive example for thermochemistry.

[70] One cannot but here turn attention to the fact that sulphur and charcoal are solids at the ordinary temperature, whilst carbon bisulphide is a very volatile liquid, and consequently, in the act of combination, referred to the ordinary temperature, there is, as it were, a passage into a liquid state, and this requires the absorption of heat. And furthermore, the molecule of sulphur contains at least six atoms, and the molecule of carbon in all probability (Chapter VIII.) a very considerable number of atoms; thus the reaction of sulphur on charcoal may be expressed in the following manner: $8C_n+nS_6=8_nCS_2$—that is, from $n+8$ molecules there proceed $3n$ molecules, and as n must be very considerable, $3n$ must be greater than $3+n$, which indicates a decomposition in the formation of carbon bisulphide, although the reaction at first sight appears as one of combination. This decomposition is seen also from the volumes in the solid and liquid states. Carbon bisulphide has a sp. gr. of 1·29; hence its molecular volume is 59. But the volume of carbon, even in the form of charcoal, is not more than 6, and the volume of S_2 is 80; hence 86 volumes after combination give 59 volumes—an expansion takes place, as in decompositions.

heated to a red heat, and then pieces of sulphur are placed in the upper end. The sulphur melts, and its vapour comes into contact with the red-hot charcoal, and combination takes place; the vapours condense in the condenser, because carbon bisulphide is a liquid boiling at 48°. On a large scale the apparatus depicted in fig. 90 is employed. A

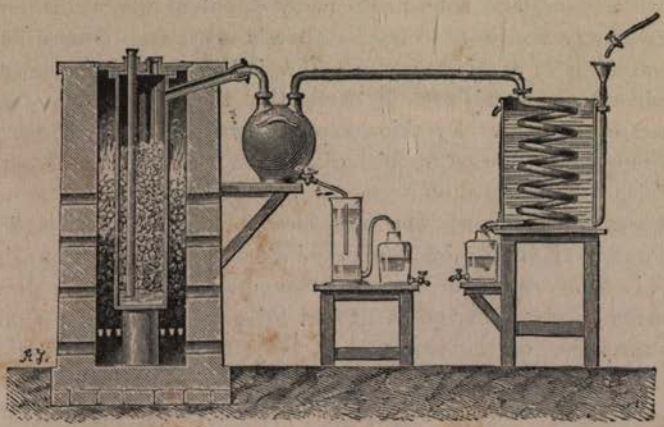


FIG. 90.—Apparatus for the manufacture of carbon bisulphide.

cast-iron cylinder rests on a stand in a furnace. Wood charcoal is charged into the cylinder through the upper tube closed by a clay stopper, whilst the sulphur is introduced through a tube reaching to the bottom of the cylinder. Pieces of sulphur thrown into this tube fall on to the bottom of the cylinder, and are converted into vapour, which passes through the entire layer of charcoal in the cylinder. The vapour of carbon bisulphide thus formed passes through the exit tube first into a Woulfe's bottle (where the sulphur which has not entered into the reaction is condensed), and then into a strongly-cooled condenser or worm.[71]

Pure carbon bisulphide is a colourless liquid, which strongly refracts light, and has a pure ethereal smell; at 0° its specific gravity is 1·293, and at 15° 1·271. If kept long it seems to undergo a change, especially

[71] It must be observed that the liquefaction of the vapours of carbon bisulphide requires a very low temperature, because its boiling-point is not high (48°), and the latent heat of evaporation is not great (about 90°). With air the vapour forms an explosive mixture which easily takes fire. Carbon bisulphide, as prepared on a large scale, is generally very impure, and contains not only sulphur, but, more especially, other impurities which give it a very disagreeable odour. The best method of purifying this malodorous carbon bisulphide is to shake it up with a certain amount of mercuric chloride, or even simply with mercury, until the surface of the metal ceases to turn black. After this the carbon bisulphide must be poured off and distilled over a water bath, after having mixed it with some oil to retain the impurities.

when it is kept under water, in which it is insoluble. It boils at 48°, and the tension of its vapour is so great that it evaporates very easily, producing cold,[72] and therefore it has to be kept in well-stoppered vessels; it is generally kept under a layer of water, which hinders its evaporation and does not dissolve it.[73]

Carbon bisulphide enters into many combinations, which are frequently closely analogous to the compounds of carbonic anhydride. In this respect it is a *thio-anhydride—i.e.*, it has an acid character, like carbonic anhydride, with the difference that the oxygen of the latter is replaced by sulphur. By thio-compounds in general are understood those compounds of sulphur which differ from the compounds of oxygen as carbon bisulphide does from carbonic anhydride—that is, which correspond with the oxygen compounds, but with substitution of sulphur for oxygen. With the sulphides of the alkalis and alkaline earths, it forms saline substances corresponding with the carbonates, and these compounds may be termed *thio-carbonates*. For example, the composition of the sodium salt Na_2CS_3 is exactly like that of sodium carbonate. They are formed by the direct solution of carbon bisulphide in aqueous solutions of the sulphides; but they are difficult to obtain in a crystalline form, because they are easily decomposable.

[72] If carbon bisulphide be evaporated under the receiver of an air-pump, or by means of a current of air, it is possible to obtain a temperature as low as −60°, and the carbon bisulphide does not solidify at this temperature. However, if a series of air-bubbles be passed through it by means of bellows, there remains a crystalline white substance which volatilises below 0°: this is a hydrate, $H_2O,2CS_2$; it easily decomposes into water and carbon bisulphide. It is formed in the above experiment by the moisture held in the air passed through the carbon bisulphide, and the fall of temperature.

[73] Strong alcohol is miscible in all proportions with carbon bisulphide, but dilute alcohol only in a definite amount, owing to its diminished solubility from the presence of the water in it. Ether, hydrocarbons, fatty oils, and many other organic substances are soluble with great ease in carbon bisulphide. This is taken advantage of in practice for extracting the fatty oils from vegetable seeds, such as linseed, &c. This is generally done by pressing the seeds under a press, but the residue always contains a certain amount of oil. These traces of oil can, however, be removed by treatment with carbon bisulphide. In this manner a solution is obtained which when heated easily parts with all the carbon bisulphide, leaving the non-volatile fatty oil behind, so that the same carbon bisulphide may be condensed and used over again for the same purpose. It also dissolves iodine, bromine, india-rubber, sulphur, and tars.

Carbon bisulphide, especially at high temperatures, very often acts with its elements in a manner in which carbon and sulphur alone are not able to react, which will be understood from what has been said above respecting its endothermal origin. If it be passed over red-hot metals—even over copper, for instance, not to mention sodium, &c.—it forms a sulphide of the metal and deposits charcoal, and if the vapour be passed over incandescent metallic oxides it forms metallic sulphides and carbonic anhydride (and sometimes a certain amount of sulphurous anhydride). Lime and similar oxides give under these circumstances a carbonate and a sulphide—for example, $CS_2 + 3CaO = 2CaS + CaCO_3$. The sulphides obtained by this means are often well crystallised, like those found in nature—for example, lead and antimony sulphides.

When the solutions of these salts are highly concentrated they begin to decompose, with the evolution of sulphuretted hydrogen and the formation of a carbonate, water taking part in the reaction—for example, $K_2CS_3 + 3H_2O = K_2CO_3 + 3H_2S$.[74]

A remarkable example[74b] of the thio-compounds is found in *thio-*

[74] If instead of a sulphide we take an alkali hydroxide, then a thiocarbonate is also formed, together with a carbonate—thus, $3BaH_2O_2 + 3CS_2 = 2BaCS_3 + BaCO_3 + 3H_2O$. From the instability of the thiocarbonates of the alkaline metals we can clearly see the reason of the difficulty with which the salts of the heavier metals are formed, whose basic properties are incomparably weaker than those of the alkali metals. However, these salts may be obtained by double decomposition. Ammonia in reacting on carbon bisulphide gives, besides products like those formed by other alkalis, a whole series of products of as complex a structure as those substances which are produced by the action of carbonic anhydride on ammonia. In the ninth chapter we examined the formation of the ammonium carbonates, and saw the transition from them into the cyanides. It is not surprising after this that the action of carbon bisulphide on ammonia not only produces the above-mentioned salts, but also amidic compounds corresponding with them, in which the oxygen is wholly or partially replaced by sulphur. Thus ammonium thiocarbimide is very easily obtained if carbon bisulphide be added to an alcoholic solution of ammonia, and the mixture cooled in a closed vessel. The salt then separates out in minute yellow crystals, $CN_2H_6S_2$.

Carbon bisulphide not only forms compounds with the metallic sulphides, but also with sulphuretted hydrogen—that is, it forms *thiocarbonic acid*, H_2CS_3. This is obtained by carefully mixing solutions of thiocarbonates with dilute hydrochloric acid. It then separates in an oily layer, which easily decomposes in the presence of water into sulphuretted hydrogen and carbon bisulphide, just as the corresponding carbonic acid (hydrate) decomposes into water and carbonic anhydride. Carbon bisulphide combines not only with sodium sulphide, but also with the bisulphide Na_2S_2, not, however, with the trisulphide Na_2S_3.

The relation of carbon bisulphide to the other carbon compounds presents many most interesting features, which are considered in organic chemistry. We will here only turn our attention to one of the compounds of this class. Ethyl sulphide, $(C_2H_5)_2S$, combines with ethyl iodide, C_2H_5I, forming a new molecule, $S(C_2H_5)_3I$. If we designate the hydrocarbon group, for instance, ethyl, C_2H_5, by Et, then the reaction would be expressed by the following equation: $Et_2S + EtI = SEt_3I$. This compound is of a saline character, corresponds with salts of the alkalis, and is closely analogous to ammonium chloride. It is soluble in water; when heated, again splits up into its components EtI and Et_2S, and with silver hydroxide gives a hydroxide, $Et_3S{\cdot}OH$, having the property of a distinct and energetic alkali, resembling caustic ammonia. Thus the compound group SEt_3 combines, like potassium or ammonium, with iodine, hydroxyl, chlorine, &c. The hydroxide $SEt_3{\cdot}OH$ is soluble in water, precipitates metallic salts, saturates acids, &c. Hence sulphur here enters into a relation towards other elements similar to that of nitrogen in ammonia and ammonium salts, with only this difference that nitrogen retains, besides iodine, hydroxyl, and other groups, also H_4 or Et_4 (for example, NH_4Cl, NEt_3HI, NEt_4I), whilst sulphur only retains Et_3. The distinctly alkaline properties of the hydroxide, triethylsulphine hydroxide, SEt_3OH, and also the sharply-defined properties of the corresponding hydroxide, tetraethylammonium hydroxide, NEt_4OH, depend naturally not only on the properties of the nitrogen and sulphur entering into their composition, but also on the large proportion of hydrocarbon groups they contain. Judging from the existence of the ethylsulphine compounds, it might be imagined that sulphur forms a compound, SH_4, with hydrogen; but no such compound is known, just as NH_5 is unknown, although NH_4Cl exists.

[74b] Thorpe and Rodger (1889), by heating a mixture of lead fluoride and phosphorus

cyanic acid—i.e. cyanic acid in which the oxygen is replaced by sulphur, HCNS. We know (Chapter IX.) that with oxygen the cyanides of the alkaline metals RCN give cyanates RCNO; but they also combine with sulphur, and therefore if yellow prussiate of potash be treated as in the preparation of potassium cyanide, and sulphur be added to the mass, then potassium thiocyanate, KNCS, is obtained in solution. This salt is much more stable than potassium cyanate; it dissolves without change in water and alcohol, forming colourless solutions from which it easily crystallises on evaporation. It may be kept exposed to air even when in solution; in dissolving in water it absorbs a considerable amount of heat, and forms a starting-point for the preparation of all the thiocyanates, RCNS, and organic compounds in which the metals are replaced by hydrocarbon groups. Such, for example, is volatile mustard oil, C_3H_5CSN (allyl thiocyanate), which gives to mustard its caustic properties. With ferric salts the thiocyanates give an exceedingly brilliant red coloration, which may serve for the discovery of the smallest traces of ferric salts in solution. Thiocyanic acid, HCNS, may be obtained by a method of double decomposition, by distilling potassium thiocyanate with dilute sulphuric acid. It is a volatile colourless liquid, having a smell recalling that of vinegar; it solidifies at 12°, is soluble in water, and may be kept in solution without change for a long time.[75]

pentasulphide to 250° in an atmosphere of dry nitrogen, obtained gaseous *phosphorus fluosulphide*, or *thiophosphoryl fluoride*, PSF_3, corresponding with $POCl_3$. This colourless gas is converted into a colourless liquid by a pressure of eleven atmospheres; it does not act on dry mercury, and takes fire spontaneously in air or oxygen, forming phosphorus pentafluoride, phosphoric anhydride, and sulphurous anhydride. It is soluble in ether, but is decomposed by water: $PSF_3 + 4H_2O = H_2S + H_3PO_4 + 3HF$ (*supra*, p. 206, Note 20).

[75] If a given compound contain more than one atom of oxygen, it may be successively replaced by sulphur. The best example of this is seen in the compound COS, in which half of the oxygen in carbonic anhydride is replaced by sulphur. This substance should be called *carbon oxysulphide*, or monothiocarbonic anhydride. This substance was obtained by Than, and is formed in many reactions. A certain amount is obtained if a mixture of carbonic oxide and the vapour of sulphur be passed through a red-hot tube. When carbon tetrachloride is heated with sulphurous anhydride, this substance is also formed; but it is best obtained in a pure form by decomposing potassium thiocyanate with a mixture of equal volumes of water and sulphuric acid. A gas is then evolved containing a certain amount of hydrocyanic acid, from which it may be freed by passing it over wool containing moistened mercuric oxide, which retains the hydrocyanic acid. It is also formed by passing the vapour of carbon bisulphide over alumina or clay heated to redness (Gautier; silicon sulphide is then formed). The pure gas has an aromatic odour, is soluble in an equal volume of water, which, however, acts on it, so that it must be collected over mercury. Its formation is expressed by the equation: $2KCNS + 2H_2O + 2H_2SO_4 = K_2SO_4 + (NH_4)_2SO_4 + 2COS$. When slightly heated, carbon oxysulphide decomposes into sulphur and carbonic oxide. It burns in air with a pale blue flame, explodes with oxygen, and yields potassium sulphide and carbonate with potassium hydroxide: $COS + 4KHO = K_2CO_3 + K_2S + 2H_2O$.

The sulphur compounds of chlorine may be regarded on the one hand as products of the metalepsis of the sulphides of hydrogen, Cl_2S and Cl_2S_2 like H_2S and H_2S_2; and on the other hand of the oxygen compounds of chlorine, because chloride of sulphur, Cl_2S, like chlorine oxide, Cl_2O, and Cl_2S_2 correspond with the higher oxide of chlorine; or thirdly, we may see in these compounds the type of the acid chloranhydrides, because they are all decomposed by water, forming hydrochloric acid, and sulphur tetrachloride, SCl_4, is decomposed, with the formation of sulphurous anhydride.[76]

The compounds of sulphur with chlorine are prepared in the apparatus depicted in fig. 91. As sulphur chloride is decomposed by water, the chlorine evolved in the flask C must be dried before coming

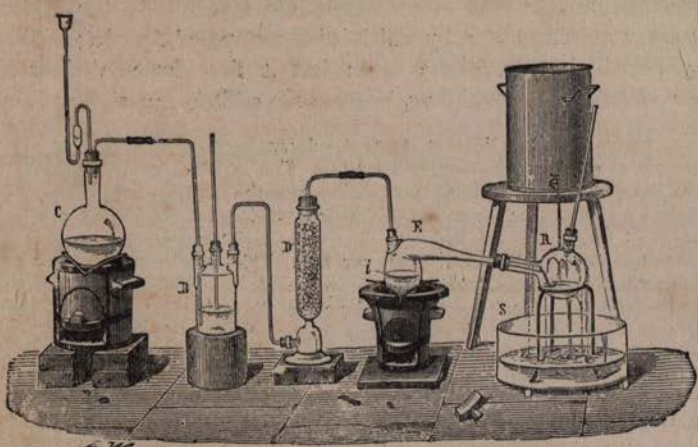


FIG. 91.—Apparatus for the preparation of sulphur chloride, and similar volatile compounds prepared by combustion in a stream of chlorine.

into contact with the sulphur. It is therefore first passed through a Woulfe's bottle, B, containing sulphuric acid, and then through the cylinder D containing pumice stone moistened with sulphuric acid, and

[76] There is no reason for seeing any contradiction or mutual incompatibility in these three views, because every analogy is more or less modified by a change of elements. Thus, for instance, it cannot be expected that the product of the metalepsis of hydrogen sulphide would resemble the same products corresponding with water in all respects, because water has not the acid properties of hydrogen sulphide. In the days of dualism and electrical polarity, it was supposed that the sulphur varied in its nature: in hydrogen sulphide or potassium sulphide it was considered to be negative, and in sulphurous anhydride or sulphur dichloride positive. It then appeared evident that sulphur dichloride would have no point of analogy with potassium sulphide. But metalepsis, or its expression in the law of substitutions, necessitates such opinions being laid aside. If we can assimilate CO_2, CH_4, CCl_4, $CHCl_3$, $CH_3(OH)$ to each other, we cannot recognise any difference in the sulphur in SH_2, SCl_2, SK_2, or SX_2, for otherwise we should have

then led into the retort E, in which the sulphur is heated. The compound which is formed distils over into the receiver, R. A certain amount of sulphur passes over with the sulphur chloride, but if the resultant distillate be re-saturated with chlorine and distilled no free sulphur remains, the boiling-point rises to 140°, and pure sulphur chloride, S_2Cl_2, is obtained. It has this formula because its vapour density referred to hydrogen is 68. It is also obtained by heating certain metallic chlorides (stannous, mercuric) with sulphur; both the metal and chlorine then combine with the sulphur. Sulphur chloride is a yellowish-brown liquid, which boils at 144°, and has a specific gravity of 1·70 at 0°. It fumes strongly in the air, reacting on the moisture contained therein, and has a heavy chloranhydrous odour. It dissolves sulphur, is miscible with carbon bisulphide, and falls to the bottom of a vessel containing water, by which it is decomposed, forming sulphurous anhydride and hydrochloric acid; but it first forms various lower stages of oxidation of sulphur, because the addition of silver nitrate to

to acknowledge as many different states of sulphur, carbon, or hydrogen as there are compounds of sulphur, or carbon, or hydrogen. The essential point of the matter is that all the elements in a molecule play their part in the reactions into which it enters. Often this appears to be contradicted in the result—for example, hydrogen alone may be replaced; but it is not this hydrogen alone that has determined the reaction, but all the elements which participated in the reaction. This may be made clearer by the following rough illustration. Supposing two regiments of soldiers were fighting against each other, and that several men were lost by one of the regiments; no one could say that it was only these men who took part in the engagement. The other men fired and the bullets flew over the heads of others. It was not only those who fell who fought, although they only were removed from the engagement, for the fighting proceeded among the masses and only a few were disabled, because they went forward and were more remarked, &c., but not because the remainder did not participate in the matter; for these acted, they were an object, they fought, only they remained whole and were not killed. Hydrogen is lighter and its atoms more mobile; it subjects itself more frequently and easily to reactions; but it is not it alone which reacts, it is even less capable of this than other elements. It participates in exceedingly diverse reactions, naturally not because the hydrogen itself varies, but because one atom of it puts itself forward, another is hidden, one is united with carbon, another feebly held by sulphur, one stands or moves near oxygen, or another unites with a hydrocarbon. All hydrogen atoms are equal, and equally serve as an object for the atoms of molecules encountering it, but those are removed from the field of battle which are nearer the surface of a molecule, which are more mobile, and held by a less sum of forces. So also sulphur is one and the same in sulphur dichloride, in sulphurous or sulphuric anhydride, in hydrogen sulphide, in potassium sulphide, but it reacts differently, and those elements which are with it also vary in their reactions because they are with it, and it varies its reactions because it is with them. It is possible to seize on a character common to substances quantitatively and qualitatively analogous to each other. It may be seen that an element in certain forms is not able to enter into reactions into which in other forms it enters willingly, if only the requisite conditions are encountered; but it cannot be thought that an element would change its tone in different cases. The preceding remarks touch on questions which are subject to much argument among chemists, and I here mention them in order to show the treatment of those most important problems of chemistry which lie at the basis of this treatise.

the solution gives a black precipitate. With hydrogen sulphide it gives sulphur and hydrochloric acid, and it reacts directly with metals—especially arsenic, antimony, and tin—forming sulphides and chlorides. In the cold, it absorbs chlorine and gives *sulphur dichloride*, SCl_2. The entire conversion into this substance requires the prolonged passage of dry chlorine through sulphur chloride surrounded by a freezing mixture. The distillation of the dichloride must be conducted in a stream of chlorine, as otherwise it partially splits up into sulphur chloride and chlorine. Pure sulphur dichloride is a reddish-brown liquid, which resembles the lower chloride in many respects; its specific gravity is 1·62; its odour is more suffocating than that of sulphur chloride; it volatilises at 64°.[77]

Thionyl chloride, $SOCl_2$, is, as it were, oxidised sulphur dichloride; it corresponds with sulphur chloride, S_2Cl_2, in which one atom of sulphur is replaced by oxygen. At the same time it is chlorine oxide (hypochlorous anhydride, Cl_2O) combined with sulphur, and also the chlor-anhydride of sulphurous acid—that is, $SO(HO)_2$—in which the two hydroxyl-groups are replaced by two atoms of chlorine, or sulphurous anhydride, SO_2, in which one atom of oxygen is replaced by two atoms of chlorine. All these representations are confirmed by reactions of formation or decomposition, they all agree with our notions of the other compounds of sulphur, oxygen, and chlorine; hence these definitions are not contradictory to each other. Thus, for instance, thionyl chloride was first obtained by Schiff, by the action of dry sulphurous anhydride on phosphorus pentachloride. On distilling the resultant liquid first thionyl chloride comes over at 80°, and then on continuing the distillation phosphorus oxychloride distils over at above 100°, $PCl_5 + SO_2$

[77] The observed vapour density of sulphur dichloride referred to hydrogen is 53·3, and that given by the formula is 51·5. The smaller molecular weight explains its boiling point being lower than that of sulphur chloride, S_2Cl_2. The reactions of both these compounds are very similar. Sulphur converts the dichloride, SCl_2, into the monochloride, S_2Cl_2. In one point the dichloride differs distinctly from the monochloride—that is, in its capacity for easily giving up chlorine and decomposing. Even light decomposes it, with the evolution of chlorine and the monochloride. Hence it acts on many substances in the same manner as chlorine, or substances which easily part with the latter, such as phosphoric or antimonic chloride. In distinction to these, however, sulphur dichloride appears to distil without any considerable decomposition, as may be judged by the vapour density. However, this is not the case. If there be a decomposition, then $2SCl_2 = S_2Cl_2 + Cl_2$, the density of sulphur chloride = 67·5, and of chlorine = 35·5; consequently a mixture of equal volumes of the two = 51·5, just the same as an equal volume of sulphur dichloride. *Therefore the distillation of sulphur dichloride is probably nothing but its decomposition.* Hence, the compound SCl_2, which is stable at the ordinary temperature, decomposes at 64°. In the cold it absorbs a further amount of chlorine in the proportion SCl_4, but even at −10° a portion of the absorbed chlorine is given off—that is, dissociation takes place. The tetrachloride is even less stable than the dichloride.

$=POCl_3+SOCl_2$. Würtz obtained the same substance by passing a stream of chlorine oxide through a cold solution of sulphur in sulphur chloride; the chlorine oxide then combined directly with the sulphur, $S+Cl_2O=SOCl_2$, whilst the sulphur chloride remained unchanged (sulphur cannot be combined directly with chlorine oxide, as an explosion takes place). Thionyl chloride is a colourless liquid, having a suffocating acrid smell; its specific gravity is 1·675 at 0°, it boils at 78°, it falls to the bottom of a vessel containing water, by which it is immediately decomposed, like all chloranhydrides—for example, like carbonyl chloride, which corresponds with it: $SOCl_2+H_2O=SO_2+2HCl$.

Normal *sulphuric acid has two corresponding chloranhydrides*; the first, $SO_2(OH)Cl$, is sulphuric acid, $SO_2(HO)_2$, in which one equivalent of HO is replaced by chlorine; the second has the composition SO_2Cl_2—that is, two HO groups are substituted by two of chlorine. The second chloranhydride, or the compound SO_2Cl_2, is called sulphuryl chloride, and the first chloranhydride, SO_2HOCl, may be called chlorosulphonic acid, because it is really an acid; it still retains one hydroxyl of sulphuric acid, and its corresponding salts are known. Thus, potassium chloride absorbs the vapour of sulphuric anhydride, forming a salt SO_3KCl, corresponding with SO_3HCl as acid. In acting on sodium chloride it forms hydrochloric acid and the salt $NaSO_3Cl$. This first chloranhydride of sulphuric acid, SO_2HOCl, discovered by Williamson, is obtained either by the action of phosphorus pentachloride on sulphuric acid ($PCl_5+H_2SO_4=POCl_3+HCl+HSO_3Cl$), or directly by the action of dry hydrochloric acid on sulphuric anhydride, $SO_3+HCl=HSO_3Cl$. The most easy and rapid method of its formation is by the direct saturation of cold Nordhausen acid with dry hydrochloric acid gas, and the distillation of the resultant solution; HSO_3Cl is then contained in the distillate. It is a colourless fuming liquid, having an acrid odour; it boils at 153° (according to my determination, confirmed by Konovaloff), and its specific gravity at 19° is 1·776. It is immediately decomposed by water, forming hydrochloric and sulphuric acids, as should be the case with a true chloranhydride. In the reactions of this chloranhydride we find the easiest means of introducing the sulphonic group (the radicle of sulphuric and sulphurous acids), HSO_3, into other compounds, because it is here combined with chlorine. The second chloranhydride of sulphuric acid, or *sulphuryl chloride*, SO_2Cl_2, was obtained by Regnault by the direct action of the sun's rays on a mixture of equal volumes of chlorine and sulphurous oxide. The gases gradually condense into a liquid, combining together as carbonic oxide does with chlorine. It is also obtained when a mixture of the two gases in acetic acid is allowed to remain for some time. The first chloranhydride,

SO_3HCl, decomposes when heated at 200° in a closed tube into sulphuric acid and sulphuryl chloride. It resembles the two above-described chloranhydrides in its properties: boils at 70°, its specific gravity is 1·70; it gives hydrochloric and sulphuric acids with water; fumes in the air, and, judging by its vapour density, it does not decompose when distilled.[78]

[78] Pyrosulphuryl chloride, $S_2O_5Cl_2$. See Note 44.

The acids of sulphur naturally have their corresponding ammonium salts, and the latter their amides and nitriles. It will be readily understood how vast a field for research is presented by the series of compounds of sulphur and nitrogen, if we only remember that to carbonic and formic acids there corresponds, as we saw (Chap. IX.), a vast series of derivatives corresponding with their ammonium salts. To sulphuric acid there correspond two ammonium salts, $SO_2(HO)(NH_4O)$ and $SO_2(NH_4O)_2$; three amides: the acid amide $SO_2(HO)(NH_2)$, or sulphamic acid, the normal saline compound $SO_2(NH_4O)(NH_2)$, or ammonium sulphamate, and the normal amide $SO_2(NH_2)_2$, or sulphamide (the analogue of urea); then the acid nitrile, $SON(HO)$, and two neutral nitriles, $SON(NH_2)$ and SN_2. There are similar compounds corresponding with sulphurous acid, and therefore its nitriles will be, an acid, $SN(HO)$, its salt, and the normal compound, $SN(NH_2)$. Dithionic and the other acids of sulphur should also have their corresponding amides and nitriles. Only a few examples are known, which we will briefly describe. Sulphuric acid forms salts of very great stability with ammonia, and ammonium sulphate is one of the commonest ammoniacal compounds. It is obtained by the direct action of ammonia on sulphuric acid, or by the action of the latter on ammonium carbonate; it separates from its solutions in an anhydrous state, like potassium sulphate, with which it is isomorphous. Hence, the composition of crystals of ammonium sulphate is $(NH_4)_2SO_4$. This salt fuses at 140°, and does not undergo any change when heated up to 180°. At higher temperatures it parts with (not water but) half its ammonia, and is converted into the acid salt, HNH_4SO_4; and this acid salt, on further heating, undergoes a further decomposition, and splits up into nitrogen, water, and acid ammonium sulphite, HNH_4SO_3. At the ordinary temperature the normal salt is soluble in twice its weight of water and at the boiling-point of water in an equal weight. In its faculty for combinations this salt exhibits a great resemblance to potassium sulphate, and, like it, easily forms a number of double salts; the most remarkable of which are the ammonia alums, $NH_4AlS_2O_8,12H_2O$, and the double salts formed by the metals of the magnesium group, having, for example, the composition $(NH_4)_2MgS_2O_8,6H_2O$. Ammonium sulphate does not give an amide when heated, perhaps owing to the faculty of sulphuric anhydride to retain the water combined with it with great force. But the amides of sulphuric acid may be very conveniently prepared from sulphuric anhydride. Their formation by this method is very easily understood, because an amide is equal to an ammonium salt less water, and if the anhydride be taken it will give an amide directly with ammonia. Thus, if dry ammonia be passed into a vessel surrounded by a freezing mixture and containing sulphuric anhydride, it forms a white mass, having the composition $SO_3,2H_3N$ and resembling the like compound of carbonic acid, $CO_2,2NH_3$. It is slowly acted on by water, and may therefore be obtained in solution, in which it slowly reacts with barium chloride, which proves that with water it still forms ammonium sulphate. This substance is naturally an ammonium salt of sulphamic acid, $SO_2(NH_4O)NH_2$. By treatment with water this substance at first gives a special deliquescent ammonium salt, containing $H_2O,2(SO_3,2NH_3)$, and then a normal ammonium salt. The compound $SO_3,2NH_3$ is known as *sulphatammon*. When freshly prepared it is powdery; it does not give a precipitate with calcium chloride, but a precipitate is obtained, although not a complete one, with barium chloride. If this substance be carefully dissolved in water and evaporated, it yields well-formed crystals, whose solution no longer gives a precipitate with barium chloride. This is not due to the pre-

In the group of the halogens we saw four closely analogous elements —fluorine, chlorine, bromine, and iodine—and we meet with a like number of closely-allied analogues in the oxygen group, because besides sulphur this group also includes *selenium* and *tellurium*: O, S, Se, Te.

sence of impurities, but to a change in the nature of the substance, and therefore Rose calls the crystalline modification *parasulphatammon*. Platinum chloride only precipitates half the nitrogen as platinochloride from solutions of sulphat- and parasulphat-ammon, which shows that they are ammonium salts, $SO_2(NH_4O)(NH_2)$. It may be that the reason of the difference in the two modifications is connected with the fact that two different substances of the composition $N_2H_4SO_2$ are possible: one is the amide $SO_2(NH_2)_2$ corresponding with the normal salt, and the other is the salt of the nitrile acid corresponding with acid ammonium sulphate—that is, $SON(ONH_4)$ corresponds with the acid $SON(OH)=SO_2(NH_4O)OH-2H_2O$. That is, there may here be a difference of the same nature as between urea and ammonium cyanate. For the present, the isomerism indicated above has been but little investigated, and might be the subject of interesting researches.

If in the preceding experiment the ammonia, and not the sulphuric anhydride, be taken in excess, then a soluble substance of the composition $2SO_3,3NH_3$ is formed. This compound, obtained by Jacqueline and investigated by Voronin, doubtless also contains a salt of sulphamic acid—that is, of the amide corresponding with the acid ammonium sulphate $= HNH_4SO_4-H_2O=(NH_2)SO_2(OH)$. Probably it is a compound of sulphat-ammon with sulphamic acid. Thus it has an acid reaction, and does not give a precipitate with barium chloride.

With normal sulphate of ammonium, an amide of the composition $N_2H_4SO_2$ should correspond, which should bear the same relation to sulphuric acid as urea bears to carbonic acid. This amide, known as *sulphamide*, is obtained by the action of dry ammonia on the sulphuryl chloride, SO_2Cl_2, which we became acquainted with above, just as urea is obtained by the action of ammonia on carbonyl chloride, $SO_2Cl_2+4NH_3=N_2H_4SO_2+2NH_4Cl$. The ammonium chloride is separated from the resultant sulphamide with great difficulty. Cold water, acting on the mixture, dissolves them both; the cold solution does not give a precipitate with barium chloride. Alkalis act on it slowly, as they do on urea; but on boiling, especially in the presence of alkalis or acids, it easily re-combines with water, and gives an ammonium salt. The action of sulphuryl chloride (and of the other chloranhydrides of sulphur) on ammonium carbonate always, as Mente showed (1888), results in the formation of the salt $NH(SO_3NH_4)_2$.

The nitriles corresponding with sulphuric acid are not as yet known with any certainty. The most simple nitrile corresponding with sulphuric acid should have the composition $N_2H_8SO_4-4H_2O=N_2S$. This would be a kind of cyanogen corresponding with sulphuric acid. On comparing sulphurous acid with carbonic acid, we saw that they present a great analogy in many respects, and therefore one would expect to also find other nitrile compounds corresponding to the cyanogen compounds already known to us, and therefore having the composition NHS and N_2S_2. The latter of these compounds is well known, and was obtained by Soubeiron, by the action of dry ammonia on sulphur chloride. This substance corresponds with cyanogen (paracyanogen), and is known as *nitrogen sulphide*, N_2S_2. It is formed according to the equation $3SCl_2+8NH_3=N_2S_2+S+6NH_4Cl$. The free sulphur and nitrogen sulphide are dissolved by acting on the product with carbon bisulphide, the nitrogen sulphide being much less soluble than the sulphur. It is a yellow, almost odourless substance, which is excessively irritating to the eyes and nostrils. It explodes when rubbed with a hard substance, being naturally decomposed with the evolution of nitrogen; but when heated it fuses without decomposing, and only decomposes with explosion at 157°. It is insoluble in water and only slightly so in alcohol, ether, and carbon bisulphide; 100 parts of the latter dissolve 1·5 parts of nitrogen sulphide at the boiling point. This solution on cooling deposits it in minute transparent prisms of a golden yellow colour.

These two groups are very closely allied, both in respect to the magnitudes of their atomic weights, and also in the faculty of the elements of both groups for combining with metals. The distinct analogy and definite degree of variance known to us for the halogens, also repeat themselves in the same degree for the elements of the oxygen group. Thus the halogens combine with H, and the elements of the oxygen group with H_2, forming H_2O, H_2S, H_2Se, H_2Te. The hydrogen compounds of selenium and tellurium are acids like hydrogen sulphide. Selenium, by simple heating in a stream of hydrogen, partially combines with it directly, but seleniuretted hydrogen is more readily decomposable by heat than sulphuretted hydrogen, and this property is still more developed in telluretted hydrogen. Hydrogen selenide and telluride are gases like sulphuretted hydrogen, and, like it, are soluble in water, form saline compounds with alkalis, precipitate metallic salts, are obtained by the action of acids on their compounds with metals, &c. Selenium and tellurium, like sulphur, give two normal grades of combination with oxygen, both of an acid character, of which only the forms corresponding to sulphurous anhydride—namely, selenious anhydride, SeO_2, and tellurous anhydride, TeO_2[79]—are formed directly.

[79] *Selenious anhydride*, SeO_2, is a volatile solid, which crystallises in prisms soluble in water. It is best procured by the action of nitric acid on selenium. The well-known researches of Nilson (1874) showed that the salts of selenious acid easily form acid salts, and are so characteristic in many respects that they may even serve for judging the analogy of types of oxides. Thus the oxides of the composition RO give normal salts of the composition $RSeO_3,2H_2O$, where R = Mn, Co, Ni, Cu, Zn. The salts of magnesium, barium, and calcium contain a different quantity of water, as also do the salts of the oxides R_2O_3. We here turn attention to the fact that beryllium gives a normal salt, $BeSeO_3,2H_2O$, and not a salt analogous to those of aluminium, scandium, $Sc_2(SeO_3)_3,H_2O$, yttrium, $Y_2(SeO_3)_3,12H_2O$, and other oxides of the form R_2O_3, which speaks in favour of the formula BeO.

Tellurous anhydride is also a colourless solid, which crystallises in octahedra; it also, when heated, first fuses and then volatilises. It is insoluble in water, and the decomposition of its salts gives a hydrate, H_2TeO_3, which is insoluble.

It is a very characteristic circumstance that selenious and tellurous anhydrides are very easily *reduced* to selenium and tellurium. This is not only effected by metals like zinc, or by sulphuretted hydrogen, which are powerful deoxidisers, but even by sulphurous anhydride, which is able to precipitate selenium and tellurium from solutions of the selenites and tellurites, and even of the acids themselves, which is taken advantage of in obtaining these elements and separating them from sulphur.

Sulphuric acid, as we know, rarely acts as an oxidising agent. It is otherwise with selenic and telluric acids, H_2SeO_4 and H_2TeO_4, which are powerful oxidising agents—that is, are easily reduced in many circumstances either into the lower oxide or even to selenium and tellurium. A powerful oxidising agent is required in order to convert selenious and tellurous anhydrides into selenic and telluric anhydrides, and, moreover, it must be taken in excess. If chlorine be passed through a solution of potassium selenide, K_2Se, telluride, K_2Te, or selenite, K_2SeO_3, or tellurite, K_2TeO_3, it acts as an oxidiser in the presence of the water, forming potassium selenate, K_2SeO_4, or tellurate, K_2TeO_4. The same salts are formed by fusing the lower oxides with nitre. These salts are isomorphous with the

These are both solids, obtained by the combustion of the elements themselves and by the action of oxidising agents on them. They form feebly energetic acids, having distinct bibasic properties; however, a characteristic difference is observable both in the physical properties of these compounds and in their stability and capacity for further oxidation, just as in the series of the halogens already known to us, only in an inverse order; in the latter we saw that iodine combines more easily than bromine or chlorine with oxygen, forming more stable oxygen compounds, whereas here, on the contrary, sulphurous anhydride, as we know, is difficultly decomposed, parts with its sulphur with difficulty, and is easily oxidised even in air and especially in its salts, while selenious and tellurous anhydrides are difficultly oxidised and easily reduced, even by means of sulphurous acid.

Selenium was obtained in 1817 by Berzelius from the sublimate which collects in the first chamber in the preparation of sulphuric acid from Fahlun pyrites. Certain other pyrites also contain small

corresponding sulphates, and cannot therefore be separated from them by crystallisation. The salts of potassium, sodium, magnesium, copper, cadmium, &c., are soluble like the sulphates, but those of barium and calcium are insoluble, in perfect analogy with the sulphates. When copper selenate, $CuSeO_4$, is treated with sulphuretted hydrogen (CuS is precipitated), *selenic acid* remains in solution. On evaporation it gives a syrupy liquid, which may be concentrated to almost the pure acid, H_2SeO_4, having a specific gravity of 2·6. Like sulphuric acid this acid attracts moisture from the atmosphere; it is not decomposed by sulphurous acid, but oxidises hydrochloric acid (like nitric, chromic, and manganic acids), evolving chlorine and forming selenious acid, $H_2SeO_4 + 2HCl = H_2SeO_3 + H_2O + Cl_2$. *Telluric acid*, H_2TeO_4, is obtained by fusing tellurous anhydride with potassium hydroxide and chlorate; the solution, containing potassium tellurate, is then precipitated with barium chloride, and the barium tellurate, $BaTeO_4$, then obtained in the precipitate is decomposed by sulphuric acid. A solution of telluric acid is thus obtained, which on evaporation yields colourless prisms, soluble in water, and containing $TeH_2O_4,2H_2O$. Two equivalents of water are driven off at 160°; on further heating the last equivalent of water is expelled, and then oxygen is given off. It also gives chlorine with hydrochloric acid, like selenic acid. Its salts also correspond with those of sulphuric acid. It must, however, be remarked that telluric and selenic acids are able to give poly-acid salts with much greater ease than sulphuric acid. Thus, for example, there are known for telluric acid not only $K_2TeO_4,5H_2O$ and $KHTeO_4,3H_2O$, but also $KHTeO_4,H_2TeO_4,H_2O = K_2TeO_4,3H_2TeO_4,2H_2O$. This salt is easily obtained from acid solutions of the preceding salts, and is less soluble in water. As selenious anhydride is volatile and gives similar poly-salts, it might be thought that selenious, tellurous, selenic, and telluric anhydrides are polymeric as compared with sulphurous and sulphuric anhydrides, for which reason it would be desirous to determine the vapour density of selenious anhydride. It would probably correspond with Se_2O_4 or Se_3O_6.

In order to show how exceedingly analogous selenium is to sulphur, I will note two examples. Potassium cyanide dissolves selenium, as it does sulphur, forming potassium selenocyanate, KCNSe, corresponding with potassium thiocyanate. Acids precipitate selenium from this solution, because selenocyanic acid, H_2CNSe, when in a free state is immediately decomposed. A boiling solution of sodium sulphite dissolves selenium, just as it would sulphur, forming a salt analogous to thiosulphate of sodium, namely, sodium selenosulphate, Na_2SSeO_3. Selenium is separated from a solution of this salt by the action of acid.

quantities of selenium. Some native selenides, especially those of lead, mercury, and copper, have been found in the Hartz Mountains, but only in small quantities. Pyrites and blendes, in which the sulphur is partially replaced by selenium, still remain the chief source for its extraction. When these pyrites are roasted they evolve selenious anhydride, which condenses in the cooler portions of the apparatus in which the pyrites are roasted, and is partially or wholly reduced by the sulphurous anhydride simultaneously formed. The presence of selenium in ores and sublimates is most simply tested by heating them before the blowpipe, when they evolve the characteristic odour of garlic. Selenium exhibits two modifications, like sulphur: one amorphous and insoluble in carbon bisulphide, the other crystalline and slightly soluble in carbon bisulphide (in 1000 parts at 45°, and 6000 at 0°), and separating from its solutions in monoclinic prisms. If the red precipitate obtained by the action of sulphurous anhydride on selenious anhydride be dried, it gives a brown powder, having a specific gravity of 4·26, which when heated changes colour and fuses into a metallic mass, which gains lustre as it cools. The selenium acquires different properties according to the rate at which it is cooled from a fused state; if rapidly cooled, it remains amorphous and has the same specific gravity (4·28) as the powder, but if slowly cooled it becomes crystalline and opaque, soluble in carbon bisulphide, and has a specific gravity of 4·80. In this form it fuses at 214° and remains unchanged, whilst the amorphous form, especially above 80°, gradually passes into the crystalline variety. The transition is accompanied by the evolution of heat, as in the case of sulphur; thus the analogy between sulphur and selenium is clearly shown here. In the fused amorphous form, selenium presents a brown mass, slightly translucent, with a vitreous fracture, whilst in the crystalline form it has the appearance of a grey metal, with a feeble lustre and a crystalline fracture. Selenium boils at 700°, forming a vapour whose density is only constant at a temperature of about 1400°, when it is equal to 79·4 (referred to hydrogen) —that is, the molecular formula is then Se_2, like sulphur at as high a temperature.

Tellurium is met with still more rarely than selenium (it is known in Saxony) in combination with gold, silver, lead, and antimony in the so-called foliated tellurium ore. Bismuth telluride and silver telluride have been found in Hungary and in the Altai. Tellurium is extracted from bismuth telluride by mixing the finely-powdered ore with potassium and charcoal in as intimate a mixture as possible, and then heating in a covered crucible. Potassium telluride, K_2Te, is then formed, because the charcoal reduces potassium tellurite.

As potassium telluride is soluble in water, forming a red-brown solution which is decomposed by the oxygen of the atmosphere ($K_2Te + O + H_2O = 2KHO + Te$), the mass formed in the crucible is treated with boiling water and filtered as rapidly as possible, and the resultant solution exposed to the air, by which means the tellurium is precipitated.[80] In a free state tellurium has a perfectly *metallic appearance*; it is of a silver-white colour, very easily crystallises in long brilliant needles; is very brittle, so that it can be easily reduced to powder; but it is a bad conductor of heat and electricity, so that in this respect, as in many others, it forms a transition from the metals to the non-metals. Its specific gravity is 6·18, it melts at an incipient red heat, and takes fire when heated in air, like selenium and sulphur, burning with a blue flame and evolving white fumes of tellurous anhydride, TeO_2, and emitting an acrid smell if no selenium be present; but if it be, its odour preponderates. Alkalis dissolve tellurium when boiled with it, potassium telluride, K_2Te, and potassium tellurite, K_2TeO_3, being formed. The solution is of a red colour, owing to the presence of the telluride, K_2Te; but the colour disappears when the solution is cooled or diluted, the tellurium being all precipitated: $2K_2Te + K_2TeO_3 + 3H_2O = 6KHO + 3Te$.[81]

[80] The tellurium thus prepared is impure, and contains a large amount of selenium. The selenium may be removed by converting their mixture into a mixture of potassium tellurate and selenate, and treating this with nitric acid and barium nitrate, when barium selenate only is precipitated, whilst the barrium tellurate remains in solution. This method does not, however, give a pure product, and it appears to be best to separate the selenium from the tellurium in a metallic form; this is done by boiling the impure potassium tellurate with hydrochloric acid, which converts it into potassium tellurite, from which the tellurium is reduced by sulphurous anhydride. The metal thus obtained is then fused and distilled in a stream of hydrogen; the selenium volatilises first, and then the tellurium, owing to its being much less volatile than the former. Nevertheless, tellurium is also volatile, and may be separated in this manner from less volatile metals, such as antimony. Brauner determined the atomic weight of pure tellurium, and found it to be 125, but he (1889) showed that tellurium purified by the usual method, even after distillation, contains a large amount of impurities.

[81] The decomposition proceeds in the above order in the cold, but in a hot solution with an excess of potassium hydroxide it proceeds inversely. A like phenomenon takes place when tellurium is fused with alkalis, and therefore it is necessary in order to obtain potassium telluride to add charcoal.

Selenium and tellurium form higher compounds with chlorine than sulphur. For selenium, $SeCl_2$ and $SeCl_4$ are known and for tellurium $TeCl_2$ and $TeCl_4$. The tetrachlorides of selenium and tellurium are formed by passing chlorine over these elements. Selenium tetrachloride, $SeCl_4$, is a crystalline, volatile mass which gives selenious anhydride and hydrochloric acid with water. Tellurium tetrachloride is much less volatile, easily fuses, and is also decomposed by water. They form similar compounds with bromine. Tellurium tetrabromide is red, fuses into a brown liquid, and volatilises, and gives a crystalline salt, $K_2TeBr_6,3H_2O$, with an aqueous solution of potassium bromide.

CHAPTER XXI

CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM, AND MANGANESE

SULPHUR, selenium, and tellurium belong to the uneven series of the sixth group. In the even series of this group there are known *chromium, molybdenum, tungsten, and uranium*; these give acid oxides of the type RO_3, like SO_3. Their acid properties are less sharply defined than those of sulphur, selenium, and tellurium, as is the case with all elements of the even series as compared with those in the uneven series in the same group. But still the oxides CrO_3, MoO_3, WO_3, and even UO_3, have clearly defined acid properties, and form salts of the composition MO,nRO_3 with bases MO. In the case of the heavy elements, and especially of uranium, the higher type of oxide, UO_3, is less acid and more basic, because in a given group of oxides the element with the highest atomic weight always acquires a more and more pronouncedly basic character. Hence UO_3 shows the properties of a base, and gives salts UO_2X_2. The basic properties of chromium, molybdenum, tungsten, and uranium are most clearly expressed in the lower oxides, which they all form. Thus chromic oxide, Cr_2O_3, is a distinct base, like alumina, Al_2O_3.

Of all these elements *chromium* is the most widely distributed and the most frequently used. It gives chromic anhydride, CrO_3, and chromic oxide, Cr_2O_3—two compounds whose relative amounts of oxygen stand in the ratio 2:1. Chromium is, although rarely, met with in nature as a compound of one or the other type. The red chromium ore of the Urals, or lead chromate, $PbCrO_4$, was the source in which chromium was discovered by Vauquelin, who gave it this name (from the Greek word signifying colour) owing to the brilliant colours of its compounds; the chromates (salts of chromic anhydride) are red and yellow, and the chromic salts (from Cr_2O_3) green and violet. The red lead chromate is, however, a rare chromium ore found only in the Urals and a few other localities. Chromic oxide, Cr_2O_3, is more frequently met with. In small quantities it forms the colouring matter of many minerals and rocks—for example, of some serpentines. The commonest

ore, and the chief source of the chromium compounds, is the *chrome iron ore*, which occurs in the Urals [1] and America, Sweden, and other localities. This is magnetic iron ore, FeO,Fe_2O_3, in which the ferric oxide is replaced by chromic oxide, its composition being FeO,Cr_2O_3. Chrome iron ore crystallises in octahedra of sp. gr. 4·4; it has a feeble metallic lustre, is of a greyish black colour, and gives a brown powder. It is very feebly acted on by acids, but when fused with potassium acid sulphate it gives a soluble mass, which contains a chromic salt, besides potassium sulphate and ferrous sulphate. In practice the treatment of chrome iron ore is mainly carried on for the preparation of chromates, and not of chromic salts, and therefore we will trace the history of the element by beginning with chromic acid, and especially with the working up of the chrome iron ore into *potassium dichromate*, $K_2Cr_2O_7$, as the most common salt of this acid. It must be remarked that chromic anhydride, CrO_3, is only obtained in an anhydrous state, and is distinguished for its capacity for easily giving anhydro-salts with the alkalis, containing one, two, and even three equivalents of the anhydride to one equivalent of base. Thus among the potassium salts there is known the normal or yellow chromate, K_2CrO_4, which corresponds to, and is perfectly isomorphous with, potassium sulphate, easily forms isomorphous mixtures with it, and is not therefore suitable for a process in which it is necessary to separate the salt from a mixture containing sulphates. As in the presence of a certain excess of acid, alkalis easily give dichromates, the object of the manufacturer is to produce such a dichromate, the more so as it contains a larger proportion of the elements of chromic acid than the normal salt. Finely-ground chrome iron ore, when heated with an alkali, absorbs oxygen almost as easily, if not more so, than a mixture of the oxides of manganese with an alkali. This absorption is due to the presence of chromic oxide, which is oxidised into the anhydride, and then combines with the alkali: $Cr_2O_3 + O_3 = 2CrO_3$. As the oxidation and formation of the chromate proceeds, the mass turns *yellow*. The iron is also oxidised, but does not give ferric acid, because the capacity of the chromium for oxidation is incomparably greater than that of the iron.

A mixture of lime and chrome iron ore is heated in a reverberatory furnace, with access of a large excess of air and at a red heat for

[1] The working of the Ural chrome iron ore into chromium compounds has been firmly established in Russia, thanks to the endeavours of P. K. Ushakoff, who constructed large works for this purpose on the river Kama, near Elabougi, where as much as 2000 tons of ore are treated yearly, owing to which the importation of chromium preparations into Russia has ceased.

several hours, until the mass becomes yellow; it then contains normal calcium chromate, $CaCrO_4$, which is insoluble in water in the presence of an excess of lime. But the calcium chromate is soluble in water in the presence of an excess of chromic acid, as may be seen from the fact that a solution of chromic acid dissolves lime. The resultant mass is ground up, and treated with water and sulphuric acid. The excess of lime forms gypsum, and the soluble calcium dichromate, $CaCr_2O_7$, together with a certain amount of iron, pass into solution. The solution is poured off, and chalk added to it; this precipitates the ferric oxide (the ferrous oxide is converted into ferric oxide in the furnace) and forms a fresh quantity of gypsum, while the chromic acid remains in solution—that is, it does not form the sparingly-soluble (1 part in 240 parts of water) normal salt. The solution then holds a fairly pure calcium dichromate, which by double decomposition gives other chromates; for example, with a solution of potassium sulphate it gives a precipitate of calcium sulphate and a solution of potassium dichromate, which crystallises when evaporated.

Potassium dichromate, $K_2Cr_2O_7$, easily crystallises from acid solutions in red, well-formed prismatic crystals, which fuse at a red heat and evolve oxygen at a very high temperature, leaving chromic oxide and the normal salt, which is not further changed: $2K_2Cr_2O_7 = 2K_2CrO_4 + Cr_2O_3 + O_3$. At the ordinary temperature 100 parts of water dissolve 10 parts of this salt, and the solubility increases as the temperature rises. It is most important to note that the dichromate does not contain water, it is $K_2CrO_4 + CrO_3$; and the acid salt corresponding to potassium acid sulphate, $KHSO_4$, does not exist. It does not even evolve heat when dissolving in water, but on the contrary produces cold; thus it does not even then form a definite compound with water. The solution and the salt itself are poisonous, and act as powerful oxidising agents, which is the character of the compounds of chromic acid in general. When heated with sulphur or organic substances, with sulphurous anhydride, hydrogen sulphide, or many metals, this salt is deoxidised, yielding chromic compounds.[2] Potassium dichromate[3] is used in the arts and in chemistry as a source for

[2] The oxidising action of potassium dichromate on organic substances at the ordinary temperature is especially marked under the action of light. Thus it acts on gelatin, as Ponton discovered; this is applied to photography in the processes of photogravure, photo-lithography, pigment printing, &c. Under the action of light this gelatin is oxidised, and the chromic anhydride deoxidised into chromic oxide, which unites with the gelatin and forms a compound insoluble in warm water, whilst, where the light has not acted, the gelatin remains soluble, its properties being unaffected by the presence of chromic acid or potassium dichromate.

[3] Ammonium and sodium dichromates are now also prepared on a large scale. The sodium salts may be prepared in exactly the same manner as those of potassium. The

the preparation of all other chromium compounds. It is converted into yellow pigments by means of double decomposition with salts of lead, barium, and zinc. When solutions of the salts of these metals are mixed with potassium dichromate (in dyeing generally mixed with soda, in order to obtain normal salts), they are precipitated as insoluble normal salts; for example, $2BaCl_2 + K_2Cr_2O_7 + H_2O = 2BaCrO_4 + 2KCl + 2HCl$. This already shows that these salts are insoluble in dilute acids, but the precipitation is not complete (as it would be with the normal salt). The barium and zinc salts are of a lemon yellow colour; the lead salt has a still more intense colour passing into orange. Yellow cotton prints are dyed with this pigment. The silver salt, Ag_2CrO_4, is of a bright red colour.

When potassium dichromate is mixed with potassium hydroxide or carbonate (carbonic anhydride is disengaged in the latter case) it forms the *normal* salt, K_2CrO_4, known as *yellow chromate* of *potassium*. Its specific gravity is 2·7, being almost the same as that of the dichromate. It absorbs heat in dissolving; one part of the salt dissolves in 1·75 parts of water at the ordinary temperature, forming a yellow solution. When mixed with even such feeble acids as acetic, not to speak of

normal salt combines with ten equivalents of water, like Glauber's salt, with which it is isomorphous. Its solution above 30° deposits the anhydrous salt. Sodium dichromate crystals contain $Na_2Cr_2O_7,7H_2O$. *The ammonium salts of chromic acid* are obtained by saturating the anhydride itself with ammonia. The dichromate is obtained by saturating one part of the anhydride with ammonia, and then adding a second part of anhydride and evaporating under the receiver of an air-pump. On ignition, the normal and acid salts leave chromic oxide. Potassium ammonium chromate, NH_4KCrO_4, is obtained in yellow needles from a solution of potassium dichromate in aqueous ammonia; it not only loses ammonia and becomes converted into potassium dichromate when ignited, but also by degrees at the ordinary temperature. This shows the feeble energy of chromic acid, and its tendency to form stable dichromates. Magnesium chromate is soluble in water, as also is the strontium salt. The calcium salt is also somewhat soluble, but the barium salt is almost insoluble. The isomorphism with sulphuric acid is evinced in the chromates by the fact that the magnesium and ammonium salts form double salts containing six equivalents of water, which are perfectly isomorphous with the corresponding sulphates. The magnesium salt crystallises in large crystals containing seven equivalents of water. The beryllium, cerium, and cobalt salts are insoluble in water. Chromic acid dissolves manganous carbonate, but on evaporation the solution deposits manganese dioxide, formed at the expense of the oxygen of the chromic acid. Chromic acid also oxidises ferrous oxide, and ferric oxide is soluble in chromic acid. It must be observed that the chromates have not yet been sufficiently investigated.

One of the chromates most used by the dyer is the insoluble yellow lead chromate, $PbCrO_4$ (*suprá*, p. 131). It easily forms a basic salt, having the composition $PbO,PbCrO_4$, as a crystalline powder, obtained by fusing the normal salt with nitre and then rapidly washing in water. The same substance is obtained, although impure and in small quantity, by treating lead chromate with potassium chromate, especially on boiling the mixture; and this gives the possibility of attaining, by means of these materials, various tints of lead chromate, from yellow to red, passing through different orange shades. The decomposition which takes place (incompletely) in this case is as follows: $2PbCrO_4 + K_2CrO_4 = PbCrO_4,PbO + K_2Cr_2O_7$—that is, potassium dichromate is formed in solution.

the ordinary acids, it gives the dichromate, and Graham obtained a trichromate, $K_2Cr_3O_{10} = K_2CrO_4, 2CrO_3$, by mixing a solution of the latter salt with an excess of nitric acid.

Chromic anhydride is obtained by preparing a saturated solution of potassium dichromate at the ordinary temperature, and pouring it in a thin stream into an equal volume of pure sulphuric acid.[4] On mixing, the temperature naturally rises; when slowly cooled, the solution deposits chromic anhydride in needle-shaped crystals of a red colour sometimes several centimetres long. The crystals are freed from the mother liquor by placing them on a porous tile. They cannot be filtered or washed, because the chromic anhydride is reduced by the filter-paper, and is dissolved during the process of washing. It is very important at this point to call attention to the fact that a hydrate of chromic anhydride is never obtained in the decomposition of chromic compounds, but always the *anhydride*, CrO_3. The corresponding hydrate, CrO_4H_2, or any other hydrate, is not even known. Nevertheless, it must be admitted that chromic acid is bibasic, because it forms salts isomorphous or perfectly analogous with the salts formed by sulphuric acid, which is the best example of a bibasic acid. It gives

[4] The sulphuric acid should not contain any lower oxides of nitrogen, because they reduce chromic anhydride into chromic oxide.

If a solution of a chromate be strongly heated with an excess of acid—for instance, sulphuric or hydrochloric acid—oxygen or chlorine is evolved, and a solution of a chromic salt is formed. Hence, under these circumstances, chromic acid cannot be obtained from its salts, although it may be obtained by many methods in a free state. One of the first methods employed consisted in converting its salts into volatile *chromium hexafluoride*, CrF_6. This compound, obtained by Unverdorben, may be prepared by mixing lead chromate with fluor spar in a dry state, and treating the mixture with fuming sulphuric acid in a platinum vessel: $PbCrO_4 + 3CaF_2 + 4H_2SO_4 = PbSO_4 + 3CaSO_4 + 4H_2O + CrF_6$. Fuming sulphuric acid is taken, and in considerable excess, because the chromium fluoride which is formed is very easily decomposed by water. It is volatile, and forms a very caustic, poisonous vapour, which condenses when cooled in a dry platinum vessel into a red, exceedingly volatile liquid, which fumes powerfully in air. The vapours of this substance when introduced into water are decomposed into hydrofluoric acid and chromic anhydride: $CrF_6 + 3H_2O = CrO_3 + 6HF$. If very little water be taken the hydrofluoric acid volatilises, and chromic anhydride separates directly in crystals. The chloranhydride of chromic acid, CrO_2Cl_2, which will be shortly described, is also decomposed in the same manner. A solution of chromic acid and a precipitate of barium sulphate are formed by treating the insoluble barium chromate with an equivalent quantity of sulphuric acid. If carefully evaporated, the solution yields crystals of chromic anhydride. Fritzsche gave a very convenient method of preparing chromic anhydride, based on the relation of chromic to sulphuric acid. At the ordinary temperature the strong acid dissolves both chromic anhydride and potassium chromate, but if a certain amount of water is added to the solution the chromic anhydride separates, and if the amount of water be increased the precipitated chromic anhydride is again dissolved. The chromic anhydride is almost all separated from the solution when it contains two equivalents of water to one equivalent of sulphuric acid. Many methods for the preparation of chromic anhydride are based on this fact.

(when heated with sodium chloride and sulphuric acid) a volatile chloranhydride, CrO_2Cl_2, containing two atoms of chlorine as a bibasic acid should.[5] Chromic anhydride is a red crystalline substance, which is converted into a black mass by heat; it fuses at 190°, and disengages oxygen above 250°, leaving a residue of chromium dioxide, CrO_2,[6] and, on still further heating, chromic oxide. Chromic anhydride

[5] Berzelius observed, and Rose carefully investigated, this remarkable reaction, which occurs between chromic acid and sodium chloride in the presence of sulphuric acid. If 10 parts of common salt be mixed with 12 parts of potassium dichromate, fused, cooled, and broken up into lumps, and placed in a retort with 20 parts of fuming sulphuric acid, it gives rise to a violent reaction, accompanied by the formation of brown fumes of *chromic chloranhydride*, or *chromyl chloride*, CrO_2Cl_2, according to the reaction: $CrO_3 + 2NaCl + H_2SO_4 = Na_2SO_4 + H_2O + CrO_2Cl_2$. The addition of an excess of sulphuric acid is necessary in order to retain the water. The same substance is always formed when a metallic chloride is heated with chromic acid, or of its salts, in the presence of sulphuric acid. The formation of this volatile substance is easily observed from the brown colour which is proper to its vapour. On condensing the vapour in a dry receiver a liquid is obtained having a sp. gr. of 1·9, boiling at 118°, and giving a vapour whose density, compared with hydrogen, is 7·9, which corresponds with the above formula. Chromyl chloride is decomposed by heat into chromic oxide, oxygen, and chlorine: $2CrO_2Cl_2 = Cr_2O_3 + 2Cl_2 + O$; so that it is able to act simultaneously as a powerful oxidising and chlorinising agent, which is taken advantage of in the investigation of many, and especially of organic, substances. When treated with water, this substance first falls to the bottom, and is then decomposed into hydrochloric and chromic acids, like all chloranhydrides: $CrO_2Cl_2 + H_2O = CrO_3 + 2HCl$. When brought into contact with inflammable substances it sets fire to them; it acts thus, for instance, on phosphorus, sulphur, oil of turpentine, ammonia, hydrogen, and other substances. It attracts moisture from the atmosphere with great energy, and must therefore be kept in closed vessels. It dissolves iodine and chlorine, and even forms a solid compound with the latter, which perhaps indicates the faculty of chromium to form its higher oxide, Cr_2O_7. The close analogy in the physical properties of the chloranhydrides, CrO_2Cl_2 and SO_2Cl_2, is very remarkable, although sulphurous anhydride is a gas, and the corresponding oxide, CrO_2, is a non-volatile solid. It may be imagined, therefore, that chromium dioxide (which will be mentioned in the following note) presents a polymerised modification of the substance having the composition CrO_2; in fact, this is obvious from the method of its formation.

If three parts of potassium dichromate be mixed with four parts of strong hydrochloric acid and a small quantity of water, and gently warmed, then it all passes into solution, and no chlorine is evolved; on cooling, the liquid deposits red prismatic crystals, known as *Peligot's salt*, which are very stable in air. This has the composition $KClCrO_3$, and is formed according to the equation $K_2Cr_2O_7 + 2HCl = 2KClCrO_3 + H_2O$. It is evident that this is the first chloranhydride of chromic acid, $HCrO_3Cl$, in which the hydrogen is replaced by potassium. It is decomposed by water, and on evaporation the solution yields potassium dichromate and hydrochloric acid. This is a fresh instance of the reversible reactions so frequently encountered. With sulphuric acid Peligot's salt forms chromyl chloride. The latter circumstance, and the fact that Geuther produced Peligot's salt from potassium chromate and chromyl chloride, give reason for thinking that it is a compound of these two substances: $2KClCrO_3 = K_2CrO_4 + CrO_2Cl_2$. It is also sometimes regarded as potassium dichromate in which one atom of oxygen is replaced by chlorine—that is, $K_2Cr_2O_6Cl_2$, corresponding with $K_2Cr_2O_7$. When heated it parts with all its chlorine, and on further heating gives chromic oxide.

[6] This is the most intermediate degree of oxidation. Chromium dioxide, CrO_2, may be obtained by mixing solutions of chromic salts with solutions of chromates. The

is exceedingly soluble in water, and even attracts moisture from the air, but, as was mentioned above, it does not form any definite compound with water. The specific gravity of its crystals is 2·7, and when fused it has a specific gravity 2·6. No heat effect is observable in the act of solution in water. The solution presents perfectly defined acid properties. It liberates carbonic anhydride from carbonates; gives insoluble precipitates of the chromates with salts of barium, lead, silver, and mercury.

The action of *hydrogen peroxide* on a solution of chromic acid or of potassium dichromate gives a *blue* solution, which very quickly becomes colourless with the disengagement of oxygen. Barreswil showed that this is due to the formation of a higher oxide of chromium, Cr_2O_7, corresponding with sulphur peroxide. This peroxide is remarkable from the fact that it very easily dissolves in ether and is much more stable in this solution, so that, by shaking up hydrogen peroxide mixed with a small quantity of chromic acid, with ether, it is possible to transfer all the blue substance formed to the ether.

With oxygen acids, chromic acid evolves oxygen; for example, with sulphuric acid the following reaction takes place: $2CrO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + O_3 + 3H_2O$. It will be readily understood from this that *a mixture of chromic acid* or *its salts with sulphuric acid* forms an excellent *oxidising agent*, which is frequently employed in chemical laboratories and even for technical purposes as a means of oxidation. Thus hydrogen sulphide and sulphurous anhydride are converted into sulphuric acid by this means. Chromic acid is able to act as a powerful oxidising agent because it passes into chromic oxide, and in so doing disengages half of the oxygen contained in it: $2CrO_3 = Cr_2O_3 + O_3$. Thus chromic anhydride itself is a powerful oxidising agent, and is therefore employed instead of nitric acid in galvanic

brown precipitate formed contains a compound, $Cr_2O_5CrO_3$, of equivalent amounts of oxides and chromic anhydrides. Probably a portion of this chromic acid remains in solution. The reaction is more clearly seen if chromic anhydride itself or a dichromate be taken. The brown precipitate of chromium dioxide contains water. The same substance is formed by the imperfect deoxidation of chromic anhydride by various reducing agents. Chromic oxide, when heated, absorbs oxygen, and appears to give the same substance. Chromic nitrate, when ignited, also gives this substance. When this substance is heated it first disengages water and then oxygen, chromic oxide being left. It corresponds with manganese dioxide, $Cr_2O_5CrO_3 = 3CrO_2$. Krüger treated chromium dioxide with a mixture of sodium chloride and sulphuric acid, and found that chlorine gas was evolved, but that chromyl chloride was not formed. Under the action of light, a solution of chromic acid also deposits the brown dioxide. At the ordinary temperature chromic anhydride leaves a brown stain upon the skin and tissues, which probably proceeds from a decomposition of the same kind. Chromic anhydride is soluble in alcohol containing water, and this solution is decomposed in a similar manner by light.

batteries (as a depolariser), the hydrogen evolved at the carbon being then oxidised, and the chromic acid converted into a non-volatile product of deoxidation, instead of yielding, as nitric acid does, volatile lower oxides of offensive odour. Organic substances are more or less perfectly oxidised by means of chromic anhydride, although this generally requires the aid of heat, and does not proceed in the presence of alkalis, but generally *in the presence of acids*. In acting on a solution of potassium iodide, chromic acid liberates iodine, six equivalents of iodine being evolved for every three equivalents of oxygen liberated; this reaction may be taken advantage of in many analyses, as the quantity of iodine may be determined with accuracy. If chromic anhydride is ignited in a stream of ammonia, it gives chromic oxide, water, and nitrogen. In all cases when chromic acid acts as an oxidising agent in the presence of acids and under the action of heat, the product of its deoxidation is a chromic salt, CrX_3, which is characterised by the green colour of its solution, so that the *red* or yellow *solution* of a salt of chromic acid is then transformed into *green solution* of a chromic salt, derived from chromic oxide, Cr_2O_3, which is closely analogous to Al_2O_3, Fe_2O_3, and other bases of the composition R_2O_3. This analogy is seen in the insolubility of the anhydrous oxide, in the gelatinous form of the colloidal hydrate, in the formation of alums, of a volatile chloride of chromium, &c.[7]

[7] As a mixture of potassium dichromate and sulphuric acid is usually employed for oxidation, the resultant solution generally contains a double sulphate of potassium and chromium—that is, *chrome alum*, isomorphous with ordinary alum—$K_2Cr_2O_7 + 4H_2SO_4 + 20H_2O = O_3 + K_2Cr_2(SO_4)_4,24H_2O$ or $2(KCr(SO_4)_2,12H_2O)$. It is prepared by dissolving potassium dichromate in dilute sulphuric acid; alcohol is then added and the solution slightly heated, or sulphurous anhydride is passed through it. On the addition of alcohol to a cold mixture of potassium dichromate and sulphuric acid, the gradual disengagement of pleasant-smelling volatile products of the oxidation of alcohol, and especially of aldehyde, C_2H_4O, is remarked. If the temperature of decomposition does not exceed 35°, a *violet* solution of chrome alum is obtained, but if the temperature be higher, a solution of the same alum is obtained of a *green* colour. As chrome alum requires for solution 7 parts of water at the ordinary temperature, it follows that if a somewhat strong solution of potassium dichromate be taken (4 parts of water and 1½ of sulphuric acid to 1 part of dichromate), it will give so concentrated a solution of chrome alum that on cooling the salt will separate without further evaporation. *If the liquid*, prepared as above or in any instance of the deoxidation of chromic acid, *be heated* (the oxidation naturally proceeds more rapidly) rather considerably, for instance, to the boiling-point of water, or if the violet solution already formed be subjected to the same temperature, then it acquires a bright *green colour*, and on evaporation the same mixture, which at lower temperatures so easily gives cubical crystals of chrome alum, does *not give any crystals whatever*. *If the green solution be kept*, however, *for several weeks* at the ordinary temperature, it deposits *violet crystals* of chrome alum. The green solution, when evaporated, gives a non-crystalline mass, and the violet crystals lose water at 100° and turn green. It must be remarked that the transition of the green modification into the violet is accompanied by a decrease in volume (Lecoq de

The reduction of chromic oxide—for instance, in solution with zinc and sulphuric acid—leads to the formation of chromous oxide, CrO, and

Boisbaudran, Favre). If the green mass formed at the higher temperature is evaporated to dryness and heated at 80° in a current of air, it does not retain more than 6 equivalents of water. Hence Löwel, and also Schrötter, concluded that the green and violet modifications of the alum depend on different degrees of combination with water, which may be likened to the different compounds of sodium sulphate with water and to the different hydrates of ferric oxide.

However, the question in this case is not so simple, as we shall afterwards see. Not chrome alum alone, but *all the chromic salts*, give two, if not three, *varieties*. At least, there is no doubt about the existence of two—a *green* and a *violet modification*. The green chromic salts are obtained by heating solutions of the violet salts, the violet solutions are produced by the prolonged keeping of solutions of the green salts. The conversion of the violet salts into green by the action of heat already indicates rather clearly the possibility of explaining the different modifications by their containing different proportions of water, and, moreover, of the green salts having a less amount of water than the violet. However, there are other explanations. Chromic oxide is a base like alumina, and is therefore able to give both acid and basic salts. It is supposed that the difference between the green and violet salts is due to this fact. This opinion of Krüger is based on the fact that alcohol separates out a salt from the green solution, which contains less sulphuric acid than the normal violet salt. On the other hand, Löwel showed that all the acid cannot be separated from the green chromic salts by suitable reagents, as easily as it can be from the same solution of the violet salts; thus barium salts do not precipitate all the sulphuric acid from solutions of the green salts. According to other researches the cause of the varieties of the chromic salts lies in a difference in the bases they contain—that is, connected with a modification of the properties of the oxide of chromium itself. However, this only refers to the hydroxides, and as hydroxides themselves are only special forms of salts, the differences observed as yet in this direction between the hydroxides only confirm the generality of the difference observed in the chromic compounds.

The salts of chromic oxide, like those of alumina, are easily decomposed, give basic and double salts, and have an acid reaction, as chromic oxide is a feeble base. Potassium and sodium hydroxides give a *precipitate* of the hydroxide with chromic salts, CrX_3. The violet and green salts give a *hydroxide soluble in an excess of the reagent*; but the hydroxide is held in solution by very feeble affinities, so that it is partially separated by heat and dilution with water, and completely so on boiling. In an alkaline solution, chromic hydroxide is easily converted into chromic acid by the action of lead dioxide, chlorine, and other oxidising agents. If the chromic oxide occurs together with such oxides as magnesia, or zinc oxide, then on precipitation it separates out from its solution in combination with these oxides, forming, for example, ZnO,Cr_2O_3. In the presence of 80 parts of ferric oxide, 100 parts of chromic oxide become insoluble in alkali hydroxides. On precipitating the violet solution of chrome alum with ammonia, a precipitate containing $Cr_2O_3,6H_2O$ is obtained, whilst in the precipitation from the boiling solution in caustic potash a hydrate containing four equivalents of water is obtained. When fused with borax chromic salts give a green glass. The same coloration is communicated to ordinary glass by the presence of traces of chromic oxide. A chrome glass containing a large amount of chromic oxide may be ground up and used as a green pigment.

In speaking of the chromium hydroxide, it is impossible not to mention *Guignet's green*, which forms one of the widely-used green pigments which have been substituted for the formerly much used poisonous arsenical copper pigments, such as Schweinfurt green. Guignet's green has an extremely bright green colour, and is distinguished for its great stability, not only under the action of light but also towards reagents; thus it is not altered by solution of alkalis, and even nitric acid does not act on it, at least not

its salts, CrX_2, of a blue colour. The further reduction of oxide of chromium and its corresponding compounds, gives *metallic chromium.*

when diluted with water. This pigment remains unchanged up to a temperature of 250°; it contains $Cr_2O_3,2HO_2$, and generally a small amount of alkali. It is prepared by fusing 8 parts of boric acid with 1 part of potassium dichromate; oxygen is disengaged, and a green glass, containing a mixture of the borates of chromium and potassium, is obtained. When cool this glass is ground up and treated with water, which extracts the boric acid and alkali, and leaves the above-named chromic hydroxide behind. This hydroxide only parts with its water at a red heat, leaving the anhydrous oxide.

The chromic hydroxides lose their water by ignition, and in doing so become spontaneously incandescent, like the ordinary ferric hydroxide (Chap. XXII.). It is not known, however, whether all the modifications of chromic oxide show this phenomenon. The anhydrous *chromic oxide*, Cr_2O_3, is exceedingly difficultly soluble in acids, if it has passed through the above recalescence. But if it has parted with its water, or the greater part of it, and not yet undergone this self-induced incandescence (has not lost a portion of its energy), then it is soluble in acids. It is not reduced by hydrogen. It is easily obtained in various crystalline forms by many methods. The chromates of mercury and ammonium give a very convenient method for its preparation, because, when ignited, they leave chromic oxide behind. In the first instance oxygen and mercury are disengaged, and in the second case nitrogen and water: $2Hg_2CrO_4 = Cr_2O_3 + O_5 + 4Hg$ or $(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2$. The second reaction is very energetic, and the mass of salt burns spontaneously if the temperature be sufficiently high. A mixture of potassium sulphate and chromic oxide is formed by heating potassium dichromate with an equal weight of sulphur: $K_2Cr_2O_7 + S = K_2SO_4 + Cr_2O_3$. The sulphate is easily extracted by water, and there remains a bright green residue of the oxide, whose colour is more brilliant the lower the temperature of the decomposition. The oxide thus obtained is used as a green pigment for china and enamel. The anhydrous chromic oxide obtained from chromyl chloride, CrO_3Cl_2, has a specific gravity of 5·21, and forms almost black crystals, which give a green powder. They are hard enough to scratch glass, and have a metallic lustre. The crystalline form of chromic oxide is identical with that of the oxide of iron and alumina, with which it is isomorphous.

The most important of the compounds corresponding with chromic oxide is *chromic chloride*, Cr_2Cl_6, which is known in an anhydrous and in a hydrated form. It resembles ferric and aluminic chlorides in many respects. There is a great difference between the anhydrous and the hydrated chlorides; the former is insoluble in water, the latter easily dissolves, and on evaporation its solution forms a hygroscopic mass, which is very unstable, and easily evolves hydrochloric acid when heated with water. The anhydrous form is of a violet colour, and Wöhler gives the following method for its preparation: an intimate mixture is prepared of the anhydrous chromic oxide with carbon and organic matter, and charged into a wide infusible glass or porcelain tube which is heated in a combustion furnace; one extremity of the tube communicates with an apparatus generating chlorine, which is passed through several bottles containing sulphuric acid in order to perfectly dry it before it reaches the tube. On heating the portion of the tube in which the mixture is placed and passing the chlorine, a slightly volatile sublimate of chromic chloride, $CrCl_3$ or Cr_2Cl_6, is formed. This substance forms *violet tabular crystals*, which may be distilled in dry chlorine without change, but which, however, require a red heat for their volatilisation. These crystals are greasy to the touch and insoluble in water, but if they be rubbed and boiled in water for a long time they pass into *a green solution.* Strong sulphuric acid does not act on the anhydrous salt, or only acts with exceeding slowness, like water. Even aqua regia and other acids do not act on the crystals, and alkalis only show a very feeble action. The specific gravity of the crystals is 2·99. When fused with sodium carbonate and nitre they give sodium chloride and potassium chromate, and when ignited in air they form green chromic oxide and evolve chlorine. When ignited in a stream of ammonia, chromic chloride forms

Deville obtained it by reducing chromic oxide with carbon, at a temperature sufficiently high to fuse platinum, but the metal itself

sal-ammoniac and chromium nitride, CrN (analogous to the nitrides BN, AlN). Mosberg and Peligot showed that when chromic chloride is ignited in hydrogen, it parts with one-third of its chlorine, forming chromous chloride, $CrCl_2$—that is, there is formed from a compound corresponding with chromic oxide, Cr_2O_3, a compound answering to the *suboxide*, chromous oxide, CrO—just as hydrogen converts ferric chloride into ferrous chloride with the aid of heat. *Chromous chloride*, $CrCl_2$, forms colourless crystals which are easily soluble in water, and in dissolving evolve a considerable amount of heat, and form a blue liquid, which is capable of absorbing oxygen from the air with great facility, and then passes into a chromic compound.

The blue solution of chromous chloride may also be obtained by the action of metallic zinc on the green solution of the hydrated chromic chloride; the zinc in this case takes up chlorine just as the hydrogen did. It must be employed in a large excess. Chromic oxide is also formed in the action of zinc on chromic chloride, and if the solution remain for a long time in contact with the zinc the whole of the chromium is converted into chromic oxychloride. Other chromic salts are also reduced by zinc into *chromous salts*, just as the ferric salts are converted into ferrous salts by it. The chromous salts are exceedingly unstable and easily oxidise and pass into chromic salts; hence the reducing power of these salts is very great. From cupric salts they separate cuprous salts, from stannous salts they precipitate metallic tin, they reduce mercuric salts into mercurous and ferric into ferrous salts. With potassium chromate they give a brown precipitate of chromium dioxide or of chromic oxide, according to the relative amounts of the substances taken: $CrO_3 + CrO = 2CrO_2$ or $CrO_3 + 3CrO = 2Cr_2O_3$. Aqueous ammonia gives a blue precipitate, and in the presence of ammoniacal salts a blue liquid is obtained which turns red in the air from oxidation. This is accompanied by the formation of compounds analogous to those given by cobalt (Chap. XXII.). A solution of chromous chloride with a hot saturated solution of sodium acetate, $C_2H_3NaO_2$, gives, on cooling, transparent red crystals of chromous acetate, $C_4H_6CrO_4,H_2O$. This salt is also a powerful reducing agent, but may be kept for a long time in a vessel full of carbonic anhydride.

The insoluble anhydrous *chromic chloride* very easily *passes into solution* in the presence of a trace (0·004) *of chromous chloride*. This remarkable phenomenon was observed by Peligot and explained by Löwel in the following manner: chromous chloride, as a lower stage of oxidation, is capable of absorbing both oxygen and chlorine, combining with various substances. It is able to decompose many chlorides by taking up chlorine from them; thus it precipitates mercurous chloride from a solution of mercuric chloride, and in so doing passes into chromic chloride: $2CrCl_2 + 2HgCl_2 = Cr_2Cl_6 + 2HgCl$. Let us suppose that the same phenomenon takes place when the anhydrous chromic chloride is mixed with a solution of chromous chloride. The latter will then take up a portion of the chlorine of the former, and pass into a soluble hydrate of chromic chloride (hydrochloride of oxide of chromium), and the original anhydrous chromic chloride will pass into chromous chloride. The chromous chloride re-formed in this manner will then act on a fresh quantity of the chromic chloride, and in this manner transfer it entirely into solution as hydrate. This view is confirmed by the fact that other chlorides, capable of absorbing chlorine like chromous chloride, also induce the solution of the insoluble chromic chloride—for example, ferrous chloride, $FeCl_2$, and cuprous chloride. The presence of zinc also aids the solution of chromic chloride, owing to its converting a portion of it into chromous chloride. The solution of chromic chloride in water obtained by these methods is perfectly identical with that which is formed by dissolving chromic hydroxide in hydrochloric acid. On evaporating the *green solution* obtained in this manner, it gives a green mass, containing water. On further heating it leaves a soluble chromic oxychloride, and when ignited it first forms an insoluble oxychloride and then chromic oxide; but no anhydrous chromic chloride, Cr_2Cl_6, is formed by heating the aqueous solution of chromic chloride, which forms an important fact in favour of the

does not fuse at this temperature. The same metal obtained by other chemists has a steel grey colour and is very hard. Bunsen obtained metallic chromium by decomposing a solution of chromic chloride, Cr_2Cl_6, by a galvanic current, as scales of a grey colour. Wöhler obtained crystalline chromium by igniting a mixture of the anhydrous chromic chloride with finely-divided zinc, and sodium and potassium

representation that the green solution of chromic chloride is nothing else but hydrochloride of oxide of chromium. At 100° the composition of the green hydrate is $Cr_2Cl_6,9H_2O$, and on evaporation crystals are obtained with 12 equivalents of water; the red mass obtained at 120° contains $Cr_2O_3,4Cr_2Cl_6,24H_2O$. The greater portion of it is soluble in water, like the mass which is formed at 150°. The latter contains $Cr_2O_3,2Cr_2Cl_6,9H_2O = 3(Cr_2OCl_4,3H_2O)$—that is, it presents the same composition as chromic chloride in which one atom of oxygen replaces two of chlorine. And if the hydrate of chromic chloride be regarded as $Cr_2O_3,6HCl$, then the substance which is obtained should be regarded as $Cr_2O_3,4HCl$ combined with water, H_2O. The addition of alkalis—for example, baryta—to a solution of chromic chloride immediately produces a precipitate, which, however, re-dissolves on shaking, owing to the formation of one of the oxychlorides just mentioned, which may be regarded as *basic salts*. Thus we may represent the product of the change produced on chromic chloride under the influence of water and heat by the following formulæ: first $Cr_2O_3,6HCl$ or $Cr_2Cl_6,3H_2O$ is formed, then $Cr_2O_3,4HCl,H_2O$ or $Cr_2OCl_4,3H_2O$, and lastly $Cr_2O_3,2HCl,2H_2O$ or $Cr_2O_2Cl_2,3H_2O$. In all three cases there are 2 equivalents of chromium to at least 3 equivalents of water. These compounds may be regarded as being intermediate between chromic hydroxide and chloride; chromic chloride is Cr_2Cl_6, the first oxychloride $Cr_2(OH)_2Cl_4$, the second $Cr_2(OH)_4Cl_2$, and the hydrate $Cr_2(OH)_6$—that is, the chlorine is replaced by hydroxyl.

It is very important to remark that the whole of the chlorine in the above compounds is not precipitated from their solutions by silver nitrate; thus the normal salt of the composition $Cr_2Cl_6,9H_2O$ only gives up two-thirds of its chlorine; therefore Peligot supposes that the normal salt contains the oxychloride combined with hydrochloric acid: $Cr_2Cl_6 + 2H_2O = Cr_2O_2Cl_2,4HCl$, and that the chlorine held as hydrochloric acid reacts with the silver, whilst that held in the oxychloride does not enter into reaction, just as we observe a very feebly-developed faculty for reaction in the anhydrous chromic chloride. Moreover, Peligot supposes that the above two oxychlorides are formed by the successive loss of first two, and then two more, molecules of hydrochloric acid. Löwel obtained the violet solution of hydrochloride of chromic oxide by decomposing the violet chromic sulphate with barium chloride. Silver nitrate precipitates all the chlorine from this violet modification; but if the violet solution be boiled and so converted into the green modification, silver nitrate then only precipitates a portion of the chlorine. These facts must naturally be taken into consideration in order to arrive at any complete decision as to the cause of the different modifications of the chromic salts. We may observe that the green modification of chromic chloride does not give double salts with the metallic chlorides, whilst the violet variety forms compounds $Cr_2Cl_6,2RCl$ (where R = an alkali metal), which are obtained by heating the chromates with an excess of hydrochloric acid and evaporating the solution until it acquires a violet colour. As the result of all the existing researches on the green and violet chromic salts, it appears to me most probable that their difference is determined by the feeble basic character of chromic oxide, by its faculty of giving basic salts, and by the colloidal properties of its hydroxide (these three properties are mutually connected), and it may therefore be said that the green modifications contain basic salts, or are the violet salts in a state of dissociation.

We may here observe that with tin the chromic salts, CrX_3, give at low temperatures CrX_2 and SnX_2, whilst at high temperatures, on the contrary, CrX_2 reduces the metal from its salts SnX_2. The reaction, therefore, belongs to the number of reversible reactions (Beketoff).

chlorides at the boiling-point of zinc. When the resultant mass has cooled the zinc may be dissolved in dilute nitric acid, and grey crystalline chromium is left behind. Frémy also prepared crystalline chromium by the action of the vapour of sodium on anhydrous chromic chloride in a stream of hydrogen, using the apparatus shown in the accompanying drawing, and placing the sodium and chromic chloride in separate

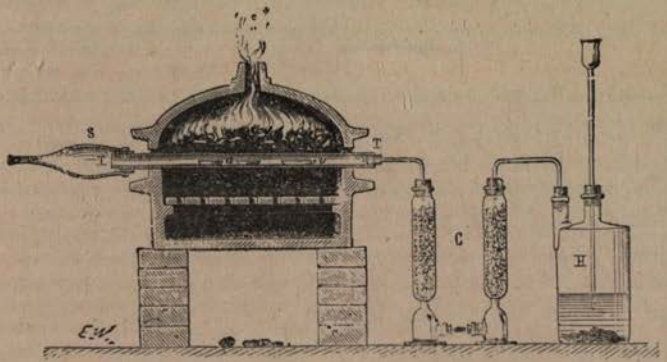


FIG. 92.—Apparatus for the preparation of metallic chromium by igniting chromic chloride and sodium in a stream of hydrogen.

porcelain boats. The tube containing these boats is only heated when it is quite full of dry hydrogen. The crystals of metallic chromium obtained in the tube are grey cubes having a considerable hardness and withstanding the action of powerful acids, and even of aqua regia. But the statements of other investigators do not entirely agree with these facts. The chromium obtained by Wöhler by the action of a galvanic current is, on the contrary, acted on under these circumstances. The reason of this difference must be looked for in the presence of impurities, and in the crystalline structure. The chromium obtained by Wöhler had a specific gravity 6·81. Other investigators give different figures.

The two analogues of chromium, *molybdenum* and *tungsten* (or wolfram), are of still rarer occurrence in nature, and form acid oxides RO_3, which are still less energetic than CrO_3. Tungsten occurs in the rather rare minerals, *scheelite*, $CaWO_4$, and *wolfram*; the latter being an isomorphous mixture of the normal tungstates of iron and manganese, $(MnFe)WO_4$. Molybdenum is most frequently met with as *molybdenite*, MoS_2, which presents a certain resemblance to graphite in its physical properties and softness. It also occurs, but much more rarely, as a yellow lead ore, $PbMoO_4$. In both these forms molybdenum occurs in the primary rocks, in granites, gneiss, &c., and in iron and copper ores in Saxony, Sweden, and Finland. Tungsten ores are some-

times met with in considerable masses in the primary rocks of Bohemia and Saxony, and also in England, America, and the Urals. The preliminary treatment of the ore is very simple; for example, the sulphide, MoS_2, is roasted, and thus converted into sulphurous anhydride and molybdic anhydride, MoO_3, which is then dissolved in alkalis, generally in ammonia. The ammonium molybdate is then treated with acids, when the sparingly soluble molybdic acid is precipitated. Wolfram is treated in a different manner. Most frequently the finely-ground ore is repeatedly boiled with hydrochloric and nitric acids, and the resultant solutions (of salts of manganese and iron) poured off, until the dark brown mass of ore disappears, whilst the tungstic acid remains, mixed with silica, as an insoluble residue; it is treated also with ammonia, and is thus converted into soluble ammonium tungstate, which passes into solution and yields tungstic acid when treated with acids. This hydrate is then ignited, and leaves tungstic anhydride. The general character of molybdic and tungstic anhydrides is analogous to that of chromic anhydride; they are anhydrides of a feebly acid character, which easily give polyacid salts.[8]

[8] The atomic composition of the tungsten and molybdenum compounds is taken as being identical with that of the compounds of sulphur and chromium, because (1) both these metals give two oxides in which the amounts of oxygen per given amount of metal stand in the ratio 2 : 3; (2) the higher oxide is of the latter kind, and, like chromic and sulphuric anhydrides, it has an acid character; (3) certain of the molybdates are isomorphous with the sulphates; (4) the specific heat of tungsten is 0·0334, consequently the product of the atomic weight and specific heat is 6·15, like that of the other elements —it is the same with molybdenum, $96·0 \times 0·0722 = 6·9$; (5) tungsten with chlorine forms not only compounds WCl_6, WCl_5 and $WOCl_4$, but also WO_2Cl_2, the analogue of chromyl chloride, CrO_2Cl_2, and sulphuryl chloride, SO_2Cl_2, a volatile substance. Molybdenum gives the chlorine compounds, $MoCl_2$, $MoCl_3$(?), $MoCl_4$ (fuses at 194°, boils at 268°; according to Debray it contains $MoCl_5$), $MoOCl_4$, MoO_2Cl_2, and $MoO_2(OH)Cl$. The existence of tungsten hexachloride, WCl_6, is an excellent proof of the fact that the type SX_6 appears in the analogues of sulphur as in SO_3; (6) the vapour density accurately determined for the chlorine compounds $MoCl_4$, WCl_6, WCl_5, $WOCl_4$ (Roscoe) leaves no doubt as to the molecular composition of the compounds of tungsten and molybdenum, because the observed and calculated results entirely agree.

Tungsten is sometimes called scheele in honour of Scheele, who discovered it in 1781 and molybdenum in 1778. Tungsten is also known as wolfram; the former name was the name given to it by Scheele, because he extracted it from the mineral then known as tungsten and now called scheelite, $CaWO_4$. The researches of Roscoe, Blomstrand, and others have subsequently thrown considerable light on the whole history of the compounds of molybdenum and tungsten.

The ammonium salts of tungstic and molybdic acids when ignited leave the anhydrides, which resemble each other in many respects. *Tungstic anhydride*, WO_3, is a yellowish substance, which only fuses at a strong heat, and has a sp. gr. of 6·2. It is insoluble in both water and acid, but solutions of the alkalis, and even of the alkali carbonates, dissolve it, especially when heated, forming alkali salts. *Molybdic anhydride*, MoO_3, is obtained by igniting the acid (hydrate) or the ammonium salt, and forms a white mass which fuses at a red heat, and solidifies to a yellow crystalline mass of sp. gr. 3·5; whilst on further heating in open vessels or in a stream of air this anhydride

Hydrogen reduces molybdic and tungstic anhydrides at a red heat; and this forms the means of obtaining metallic molybdenum and

sublimes in pearly scales—this enables it to be obtained in a pretty pure state. Water dissolves it in small quantities—namely, 1 part requires 600 parts of water for its solution. The hydrates of molybdic anhydride are *soluble also in acids* (a hydrate, H_2MoO_4, is obtained from the nitric acid solution of the ammonium salt), which forms one of their distinctions from the tungstic acids. But after ignition molybdic anhydride is insoluble in acids, like tungstic anhydride; alkalis dissolve this anhydride, easily forming molybdates. Potassium bitartrate dissolves the anhydride with the aid of heat. None of the acids yet considered by us form so many different salts with one and the same base (alkali) as molybdic and tungstic acids. The composition of these salts, and their properties also, vary considerably. The most important discovery in this respect was made by Marguerite and Laurent, who showed that the salts, which contain a large proportion of tungstic acid, are easily soluble in water, and ascribed this property to the fact that tungstic acid may be obtained *in several states*. The common tungstates, obtained with an excess of alkali, have an alkaline reaction, and on the addition of sulphuric or hydrochloric acid first deposit an acid salt and then a hydrate of tungstic acid, which is insoluble in both water and acids; but if instead of sulphuric or hydrochloric acids, we add acetic or phosphoric acid, or if the tungstate be saturated with a fresh quantity of tungstic acid, which may be done by boiling the solution of the alkali salt with the precipitated tungstic acid, then a solution is obtained which, on the addition of sulphuric or a like acid, does not give a precipitate of tungstic acid at the ordinary or a higher temperature. The solution then contains particular salts of tungstic acid, and if there is an excess of acid it also contains tungstic acid itself; Laurent, Riche, and others called it *metatungstic acid*, and it is still known by this name. Those salts which with acids immediately give the insoluble tungstic acid have the composition R_2WO_4, $RHWO_4$, whilst those which give the soluble metatungstic acid contain a far greater proportion of the acid elements. Scheibler obtained the (soluble) metatungstic acid itself by treating the soluble barium (meta) tetratungstate, $BaO,4WO_3$, with sulphuric acid. Subsequent research showed the existence of a similar phenomenon for molybdic acid. There is no doubt that this is a case of colloidal modifications.

Many chemists have occupied themselves with the investigation of the various salts formed by molybdic and tungstic acids. The tungstates have been investigated by Marguerite, Laurent, Marignac, Riche, Scheibler, Anthon, and others. The molybdates were partially studied by the same chemists, but chiefly by Struve and Svanberg, Delafontaine, and others. It appears that for a given amount of base the salts contain one to eight equivalents of molybdic or tungstic anhydride; *i.e.*, if the base have the composition RO, then the highest proportion of base will be held by the salts of the composition $ROWO_3$ or $ROMoO_3$—that is, in those salts which correspond with the normal acids H_2WO_4 and H_2MoO_4, of the same nature as sulphuric acid; but there also exist salts of the composition $RO,2WO_3$, $RO,8WO_3$ . . . . $RO,8WO_3$. The water contained in the composition of many of the acid salts is often not taken into account in the above. The properties of the salts holding different proportions of acid vary considerably, but one salt may be converted into another by the addition of acid or base with great facility, and the greater the proportion of the elements of the acid in a salt, the more stable, within a certain limit, is its solution and the salt itself.

The most common ammonium molybdate has the composition $(NH_4HO)_6,H_2O,7MoO_3$ (or, according to Marignac and others, NH_4HMoO_4). It is prepared by evaporating an ammoniacal solution of molybdic acid. It is used in the laboratory for precipitating phosphoric acid. It is purified for this purpose by mixing its solution with a small quantity of magnesium nitrate, in order to precipitate any phosphoric acid present, filtering, and then adding nitric acid and evaporating to dryness. A pure ammonium molybdate free from phosphoric acid may then be extracted from the residue.

Phosphoric acid forms insoluble compounds with the oxides of uranium and iron, tin,

tungsten. *Both metals* are infusible. Molybdenum forms a grey powder, which scarcely aggregates under a most powerful heat, and has

bismuth, &c., having feeble basic and even acid properties. This perhaps depends on the fact that the atoms of hydrogen in phosphoric acid are of a very different character, as we saw above. Those atoms of hydrogen which are difficultly replaced by ammonium, sodium, &c., are probably easily replaced by feebly energetic acid groups—that is, the formation of particular complex substances may be expected to take place at the expense of these atoms of the hydrogen of phosphoric acid and of certain feeble metallic acids; and these substances will still be acids, because the hydrogen of the phosphoric acids and metallic acids, which is easily replaced by metals, is not removed by their mutual combination, but remains in the resultant compound. Such a conclusion is verified in the *phosphomolybdic acids* obtained (1888) by Debray. If a solution of ammonium molybdate be acidified, and a small amount of a solution (it may be acid) containing orthophosphoric acid or its salts be added to it (so that there are at least 40 parts of molybdic acid present to 1 part of phosphoric acid), then after a period of twenty-four hours the whole of the phosphoric acid is separated as a yellow precipitate, containing, however, not more than 3 to 4 p.c. of phosphoric anhydride, about 3 p.c. of ammonia, about 90 p.c. of molybdic anhydride, and about 4 p.c. of water. The formation of this precipitate is so distinct and so complete that this method is employed for the discovery and separation of the smallest quantities of phosphoric acid. Phosphoric acid was found to be present in the majority of rocks by this means. The precipitate is soluble in ammonia and its salts, in alkalis and phosphates, but is perfectly insoluble in nitric, sulphuric, and hydrochloric acids in the presence of ammonium molybdate. The composition of the precipitate appears to vary under the conditions of its precipitation, but its nature became clear when the acid corresponding with it was obtained. If the above-described yellow precipitate be boiled in aqua regia, then the ammonia is destroyed, and an acid is obtained in solution, which, when evaporated in the air, crystallises out in yellow oblique prisms of approximately the composition $P_2O_5,20MoO_3,26H_2O$. Such an unusual proportion of component parts is explained by the above-mentioned considerations. In reality, molybdic acid easily gives salts $R_2O nMoO_3 mH_2O$, which we may imagine to correspond to a hydrate $MoO_2(HO)_2 nMoO_3 mH_2O$. And suppose that such a hydrate reacts on orthophosphoric acid, forming water and compounds of the composition $MoO_2(HPO_4)nMoO_3mH_2O$ or $MoO_3(H_2PO_4)_2nMoO_3mH_2O$; this is actually the composition of phosphomolybdic acid. Probably it contains a portion of the hydrogen replaceable by metals of both the acids H_3PO_4 and of H_2MoO_4. The above-cited crystalline acid is probably $H_3MoPO_7,9MoO_3,12H_2O$. This acid is really tribasic, because its aqueous solution precipitates salts of potassium, ammonium, rubidium (but not lithium and sodium) *from acid solutions*, and gives a *yellow* precipitate of the composition $R_3MoPO_7,9MoO_3,3H_2O$, where $R=NH_4$. Besides these, salts of another composition may be obtained, as would be expected from the preceding. These salts are only stable in acid solutions (which is naturally due to their containing an excess of acid oxides), whilst under the action of alkalis they give *colourless* phosphomolybdates of the composition $R_3MoPO_7,MoO_2,3H_2O$. The corresponding salts of potassium, silver, ammonium, are easily soluble in water and crystalline.

For tungstic acid there are known: (1) Normal salts—for example, K_2WO_4; (2) the so-called acid salts have a composition like $3K_2O,7WO_3,6H_2O$ or $K_6H_8(WO_4)_7,2H_2O$; (3) the tritungstates like $Na_2O,3WO_3,3H_2O=Na_2H_4(WO_4)_3,H_2O$. All these three classes of salts are soluble in water, but are precipitated by barium chloride, and with acids in solution give an insoluble hydrate of tungstic acid; whilst those salts which are enumerated below do not give a precipitate either with acids or the salts of the heavy metals, because they form soluble salts with even barium and lead. They are generally called metatungstates. They all contain water and a larger proportion of acid elements than the preceding salts; (4) the tetratungstates, like $Na_2O,4WO_3,10H_2O$ and $BaO,4WO_3,9H_2O$, for example; (5) the octatungstates—for example, $Na_2O,8WO_3,24H_2O$. As the metatung-

a specific gravity of 8·6. It is not acted on by the air at the ordinary temperature, but when ignited it is first converted into a brown, and

states, at 100°, lose so much water that they leave salts whose composition corresponds with an acid, $3H_2O,4WO_3$—that is, $H_6W_4O_{15}$—it is supposed, although without much ground, that these salts contain a particular soluble metatungstic acid of the composition $H_6W_4O_{15}$. This would be likely if there were actually known to exist salts $3R_2O,4WO_3 = R_6W_4O_{15}$, giving a soluble tungstic acid, but even those in which the ratio is $2Na_2O : 4WO_3$ already give an insoluble tungstic acid, and a small quantity of alkali converts the meta-salts into the ordinary salts.

As an example we will proceed to give a short description of the sodium salts. The normal salt, Na_2WO_4, is obtained by heating a strong solution of sodium carbonate with tungstic acid to a temperature of 80°; if the solution be filtered hot, it crystallises in rhombic tabular crystals, having the composition $Na_2WO_4,2H_2O$, which remain unchanged in the air and are easily soluble in water. When this salt is fused with a fresh quantity of tungstic acid, it gives a ditungstate, which is soluble in water and separates from its solution in crystals containing water. The same salt is obtained by carefully adding hydrochloric acid to the solution of the normal salt so long as a precipitate does not appear, and the liquid still has an alkaline reaction. This salt was first supposed to have the composition $Na_2W_2O_7,4H_2O$, but it has since been found to contain (at 100°) $Na_6W_7O_{24},16H_2O$—that is, it corresponds with the like salt of molybdic acid.

(If this salt be heated to a red heat in a stream of hydrogen, it loses a portion of its oxygen, acquires a metallic lustre, and turns a golden yellow colour, and, after being treated with water, alkali, and acid, leaves golden yellow leaflets and cubes which are very like gold. This very remarkable substance, discovered by Wöhler, has, according to Malaguti's analysis, the composition $Na_2W_3O_9$; that is, it, as it were, contains a double tungstate of tungsten oxide, WO_2, and of sodium, Na_2WO_4,WO_2WO_3. The decomposition of the fused sodium salt is best effected by finely-divided tin. This substance has a sp. gr. 6·6; it conducts electricity like metals, and like them has a metallic lustre. When brought into contact with zinc and sulphuric acid it disengages hydrogen, and it becomes coated with a coating of copper in a solution of copper sulphate in the presence of zinc—that is, notwithstanding its complex composition, it presents to a certain extent the appearance and reactions of the metals. It is not acted on by aqua regia or alkaline solutions, but it is oxidised when ignited in air.)

The ditungstate mentioned above, deprived of water (having undergone a modification similar to that given by metaphosphoric acid), after being treated with water, leaves an anhydrous, sparingly soluble tetratungstate, $Na_2WO_4,3WO_3$, which, when heated at 120° in a closed tube with water, passes into an easily soluble metatungstate. This clearly shows that the metatungstates are hydrated compounds. On boiling a solution of the above-mentioned salts of sodium with the yellow hydrate of tungstic acid they give a solution of metatungstate, which is the hydrated tetratungstate. Its crystals contain $Na_2W_4O_{13},10H_2O$. After the hydrate of tungstic acid (obtained from the ordinary tungstates by precipitation with an acid) has stood a long time in contact with a solution (hot or cold) of sodium tungstate (the yellow precipitate of the hydrate passes into a white sodium salt), it gives a solution which is not precipitated by hydrochloric acid; this must be filtered and evaporated over sulphuric acid in a desiccator (it is decomposed by boiling). It first forms a very dense solution (aluminium floats in it) of sp. gr. 3·0, and octahedral crystals of *sodium metatungstate*, $Na_2W_4O_{13},10H_2O$, sp. gr. 3·85, then separate. It effloresces and loses water, and at 100° only two out of the ten equivalents of water remain, but the properties of the salt remain unaltered. If the salt be deprived of water by further heating, it becomes insoluble. At the ordinary temperature one part of water dissolves ten parts of the metatungstate. The other metatungstates are easily obtained from this salt. Thus a strong and hot solution, mixed with a like solution of barium chloride, on cooling gives crystals of barium metatungstate, $BaW_4O_{13},9H_2O$. These crystals are dissolved without change in water containing hydrochloric acid, also in hot water, but they are

then into a blue oxide, and lastly into molybdic anhydride. Acids do not act on it—that is, it does not disengage hydrogen with them, not

partially decomposed by cold water, with the formation of a solution of metatungstic acid and of the normal barium salt, $BaWO_4$.

In order to explain the difference in the properties of the salts of tungstic acid, we may add that a mixture of a solution of tungstic acid with a solution of silicic acid does not coagulate when heated, although the silicic acid alone would do so; this is due to the formation of a silicotungstic acid, discovered by Marignac. A solution of a tungstate dissolves gelatinous silica, just as it does gelatinous tungstic acid, and when evaporated deposits a crystalline salt of silicotungstic acid. This solution is not precipitated by either acids (a clear analogy to the metatungstates) or sulphuretted hydrogen, and corresponds with a series of salts. These salts contain an equivalent of silica and 8 equivalents of hydrogen or metals, in the same form as in salts, to 12 or 10 equivalents of tungstic anhydride; for example, the crystalline potassium salt has the composition $K_8W_{12}SiO_{42},14H_2O = 4K_2O,12WO_3,SiO_2,14H_2O$. Acid salts are also known in which half of the metal is replaced by hydrogen. Gibbs studied many of these complex inorganic acids containing tungstic (molybdic and phosphoric) acid. Their complexity (for example, of the phosphomolybdic acid) involuntarily leads to the idea of polymerisation, which we were obliged to recognise for silica, lead oxide, and other compounds. This polymerisation, it seems to me, may be understood thus: a hydrate A (for example, tungstic acid) is capable of combining with a hydrate B (for example, silica or phosphoric acid, with or without the disengagement of water), and by reason of this faculty it is capable of polymerisation—that is, A combines with A—combines with itself—just as aldehyde, C_2H_4O, or the cyanogen compounds are able to combine with hydrogen, oxygen, &c., and are liable to polymerisation. In this sense the molecule of tungstic acid is probably much more complex than we represent it; this agrees with the easy volatility of such compounds as the chloranhydrides, CrO_2Cl_2, MoO_2Cl_2, the analogues of the volatile sulphuryl chloride, SO_2Cl_2, and with the non-volatility, or difficult volatility, of chromic and molybdic anhydrides, the analogues of the volatile sulphuric anhydride. Such a view also finds a certain confirmation in the researches made by Graham on the *colloidal* state of tungstic acid, because colloidal properties only appertain to compounds of a very complex composition. The observations made by Graham on the colloidal state of tungstic and molybdic acids introduced much new matter into the history of these substances. When sodium tungstate, mixed in a dilute solution with an equivalent quantity of dilute hydrochloric acid, is put in a dialyser, hydrochloric acid and sodium chloride pass through the membrane, and a solution of tungstic acid remains in the dialyser. Out of 100 parts of tungstic acid about 80 parts remain in the dialyser. The solution has a bitter, astringent taste, and does not yield gelatinous tungstic acid (hydrogel) either when heated or on the addition of acids or salts. It may also be evaporated to dryness; it then forms a vitreous mass of the *hydrosol* of *tungstic acid*, which adheres strongly to the walls of the vessel in which it has been evaporated, and is perfectly soluble in water. It does not even lose its solubility after having been heated to 200°, and only becomes insoluble when heated to a red heat, when it loses about 2½ p.c. of water. The dry acid, dissolved in a small quantity of water, forms a gluey mass, just like gum arabic, which is one of the representatives of the hydrosols of colloidal substances. The solution, containing 5 p.c. of the anhydride, has a sp. gr. of 1·047; with 20 p.c., of 1·217; with 50 p.c., of 1·80; and with 80 p.c., of 3·24. A similar stable solution of molybdic acid is obtained by the dialysis of a mixture of a strong solution of sodium molybdate with hydrochloric acid (the precipitate which is formed is re-dissolved). The addition of alkali to the solutions of the hydrosols of tungstic and molybdic acids immediately results in the re-formation of the ordinary tungstates and molybdates. There appears to be no doubt but that the same transformation is accomplished in the passage of the ordinary tungstates into the metatungstates as takes place in the passage of tungstic acid itself from an insoluble into a

even with hydrochloric acid—but strong sulphuric acid disengages sulphurous anhydride, forming a brown mass, containing a lower oxide of molybdenum. Alkalis in solution do not act on molybdenum, but when fused with it hydrogen is given off, which shows, as does its whole character, the acid properties of the metal. The properties of tungsten are almost identical ; it is infusible, has an iron grey colour, is exceedingly hard, so that it even scratches glass. Its sp. gr. is 19·1 (according to Roscoe), so that, like uranium, platinum, &c., it is one of the heaviest metals.[9]

Uranium, U=240, has the highest atomic weight of all the analogues of chromium, and indeed of all the elements yet known. Its highest salt-forming oxide, UO_3, shows very feeble acid properties. Although with alkalis it gives sparingly-soluble yellow compounds, which fully correspond with the dichromates—for example, $Na_2U_2O_7 = Na_2O,2UO_3$,[10]—yet it more frequently and easily reacts with acids HX,

soluble state; but this may be even actually proved to be the case, because Scheibler obtained a solution of tungstic acid, before Graham, by decomposing barium metatungstate with sulphuric acid. By treating this salt with sulphuric acid in the amount required for the precipitation of the baryta, Scheibler obtained a solution of metatungstic acid which, when containing 43·75 p.c. of acid, had a sp. gr. of 1·634, and with 27·61 p.c. a sp. gr. of 1·327—that is, specific gravities corresponding with those found by Graham.

The questions in conjunction with the metamorphosis or modifications of tungstic and molybdic acids, and the polymerisation and colloidal state of substances, belongs to that class of alternatives the solution of which will do much towards attaining a true comprehension of the mechanism of a number of chemical reactions. I think, moreover, that questions of this kind stand in intimate connection with the theory of the formation of solutions and alloys and other so-called indefinite compounds.

[9] We may conclude our description of tungsten and molybdenum by stating that their sulphur compounds have an acid character, like carbon bisulphide or stannic sulphide. If sulphuretted hydrogen be passed through a solution of a molybdate it does not give a precipitate unless sulphuric acid be present, when a dark brown precipitate of *molybdenum trisulphide*, MoS_3, is formed. When this sulphide is ignited without access of air it gives the bisulphide MoS_2, which is not able to combine with potassium sulphide like the trisulphide MoS_3, which forms a salt, K_2MoS_4, corresponding with K_2MoO_4. This is soluble in water, and separates out from its solution in red crystals, which have a metallic lustre and reflect a green light. It is easily obtained by heating the native bisulphide, MoS_2, with potash, sulphur, and a small amount of charcoal, which serves for deoxidising the oxygen compounds. Tungsten gives similar compounds, R_2WS_4, where $R=NH_4$, K, Na. They are decomposed by acids, with the separation of tungsten trisulphide, WS_3, and molybdenum trisulphide, MoS_3.

[10] Uranium trioxide, or uranic oxide, shows its feeble basic and acid properties in a great number of its relations. (1) Solutions of uranic salts give yellow precipitates with alkalis, but these precipitates do not contain the hydrate of the oxide, but compounds of it with bases; for example, $2UO_2(NO_3)_2 + 6KHO = 4KNO_3 + 3H_2O + K_2U_2O_7$. There are other *urano-alkali compounds* of the same constitution; for example, $(NH_4)_2U_2O_7$ (known in trade as uranic oxide), MgU_2O_7, BaU_2O_7. They are the analogues of the dichromates. Sodium uranate is the most generally used under the name of uranium yellow, $Na_2U_2O_7$. It is used for imparting the characteristic yellow-green tint to glass and porcelain. Neither heat nor water nor acids are able to extract the alkali from

forming fluorescent yellowish green salts of the composition UO_2X_2, and in this respect uranic trioxide, UO_3, differs from chromic anhydride, CrO_3, although the latter is able to give the oxychloride, CrO_2Cl_2. In molybdenum and tungsten, however, we see a clear transition from chromium to uranium. Thus, for example, chromyl choride, CrO_2Cl_2, is a brown liquid which volatilises without change, and is completely decomposed by water; molybdenum oxychloride, MoO_2Cl_2, is a crystalline substance of a yellow colour, which is volatile and soluble in water (Blomstrand), like many salts. Tungsten oxychloride, WO_2Cl_2, stands still nearer to uranyl chloride in its properties; it forms yellow scales on which water and alkalis act, as they do on many salts

sodium uranate, $Na_2U_2O_7$, and therefore it is a true insoluble salt, of a yellow colour, and clearly indicates the acid character (although feeble) of uranic oxide. (2) The carbonates of the alkaline earths (for instance, barium carbonate) precipitate uranic oxide from its salts, as they do all the salts of feeble bases; for example, R_2O_3. (3) The *alkali carbonates*, when added to solutions of uranic salts, give a *precipitate, which is soluble in an excess of the reagent*, and particularly so if the acid carbonates be taken. This is due to the fact that (4) the uranyl salts *easily form double salts* with the salts of the alkali metals, including the salts of ammonium. Uranium, in the form of these double salts, often gives salts of well-defined crystalline form, although the simple salts are little prone to appear in crystals. Such are, for example, the salts obtained by dissolving potassium uranate, $K_2U_2O_7$, in acids, with the addition of potassium salts of the same acids. Thus, with hydrochloric acid and potassium chloride a well-formed crystalline salt, $K_2(UO_2)Cl_4,2H_2O$, belonging to the monoclinic system, is produced. This salt decomposes in dissolving in pure water. Among these double salts we may mention the double carbonate with the alkalis, $R_4(UO_2)(CO_3)_3$ (they are equal to $2R_2CO_3 + UO_2CO_3$); the acetates, $R(UO_2)(C_2H_3O_2)_3$—for instance, the sodium salt, $Na(UO_2)(C_2H_3O_2)_3$, and the potassium salt, $K(UO_2)(C_2H_3O_2)_3,H_2O$; the sulphates, $R_2(UO_2)(SO_4)_2,2H_2O$, &c. In the preceding formula R = K, Na, NH_4, or R_2 = Mg, Ba, &c. *This property of giving comparatively stable double salts indicates feebly developed basic properties*, because double salts are mainly formed by salts of distinctly basic metals (this forms, as it were, the basic element of a double salt) and salts of feebly energetic bases (this forms the acid element of a double salt), just as the former also give acid salts; the acid of the acid salts is replaced in the double salts by the salt of the feebly energetic base, which, like water, belongs to the number of intermediate bases. For this reason barium does not give double salts with alkalis as magnesium does, and this is why double salts are more easily formed by potassium than by lithium among the series of the alkali metals. (5) The most remarkable property, proving the feeble energy of uranic oxide as a base, is seen in the fact that when compared with the composition of other salts the salts of uranic oxide *always appear as basic salts*. We already know that a normal salt, R_2X_6, corresponds with the oxide R_2O_3, where X = Cl, NO_3, &c., or $X_2 = SO_4$, CO_3, &c.; but there also exist basic salts of the same type where X = HO or X_2 = O. We saw salts of all kinds among the salts of aluminium, chromium, and others. With uranic oxide no salts are known of the types UX_6 (UCl_6, $U(SO_4)_3$, alums, &c., are not known), nor even salts, $U(HO)_2X_4$ or UOX_4, but it always forms salts after the type $U(HO)_4X_2$ or UO_2X_2. Judging from the fact that nearly all the salts of uranic oxide retain water in crystallising from their solutions, and that this water is difficult to separate from them, it may be thought to be water of hydration. This is seen in part from the fact that the composition of many of the salts of uranic oxide may then be expressed without the presence of water of crystallisation; for instance, $U(HO)_4K_2Cl_4$ (and the salt of NH_4), $U(HO)_4K_2(SO_4)_2$, $U(HO)_4(C_2H_3O_2)_2$. Sodium uranyl acetate, however, does not contain water.

(zinc chloride, ferric chloride, aluminium chloride, stannic chloride, &c.), and perfectly corresponds with the difficultly-volatile salt, UO_2Cl_2 (obtained by Peligot by the action of chlorine on ignited uranium dioxide, UO_2), which is also yellow and gives a yellow solution with water, like all the salts UO_2X_2. The property of uranic oxide, UO_3, of forming salts UO_2X_2 is shown in the fact that the hydrated oxide of uranium, $UO_2(HO)_2$, which is obtained from the nitrate, carbonate, and other salts by the loss of the elements of the acid, is easily soluble in acids, as well as in the fact that the lower grades of oxidation of uranium are able, when treated with nitric acid, to form an easily crystallisable uranyl nitrate, $UO_2(NO_3)_2,6H_2O$; this is the most commonly occurring uranium salt.[11]

[11] *Uranyl nitrate*, or uranium nitrate, $UO_2(NO_3)_2,6H_2O$, crystallises from its solutions in transparent yellowish-green prisms (from an acid solution), or in tabular crystals (from a neutral solution), which effloresce in the air and are easily soluble in water, alcohol, and ether, have a sp. gr. of 2·8, and fuse when heated, losing nitric acid and water in the process. If the salt itself (Berzelius) or its alcoholic solution (Malaguti) be heated up to the temperature at which oxides of nitrogen are evolved, then there remains a mass which, after being evaporated with water, leaves uranyl hydroxide, $UO_2(HO)_2$ (sp. gr. 5·93), whilst if the salt be ignited there remains the dioxide, UO_2, as a brick-red powder, which on further heating loses oxygen and forms the dark olive uranoso-uranic oxide, U_3O_8. Therefore the solution of the nitrate obtained from the ore is purified in the following manner: sulphurous anhydride is first passed through it in order to reduce the arsenic acid present into arsenious acid; the solution is then heated to 60°, and sulphuretted hydrogen passed through it; this precipitates the lead, arsenic, and tin, and certain other metals, as sulphides, insoluble in water and dilute nitric acid. This liquid is then filtered and evaporated with nitric acid to crystallisation, and the crystals are dissolved in ether. Or else the solution is first treated with chlorine in order to convert the ferrous chloride (produced by the action of the hydrogen sulphide) into ferric chloride, then the oxides are precipitated by ammonia and the resultant precipitate, containing the oxides Fe_2O_3,UO_3, and compounds of the latter with potash, lime, ammonia, and other bases present in the solution (the latter is due to the property of uranic oxide of combining with bases), is washed and dissolved in a strong, slightly-heated solution of ammonium carbonate, which dissolves the uranic oxide but not the ferric oxide. The solution is filtered, and on cooling deposits a finely crystallising *uranyl ammonium carbonate*, $UO_2(NH_4)_4(CO_3)_3$, in brilliant monoclinic crystals which on exposure to air slowly give off water, carbonic anhydride, and ammonia; the same decomposition is readily effected at 300°, the residue then consisting of uranic oxide. This salt is not very soluble in water, but is readily so in ammonium carbonate; it is obvious that it may readily be converted into all the other salts of oxides of uranium. Uranium salts are also purified in the form of *acetate*, which is very sparingly soluble, and is therefore directly precipitated from a strong solution of the nitrate by mixing it with acetic acid.

We may also mention the *uranyl phosphate*, $HUPO_6$, which must be regarded as an orthophosphate in which two hydrogens are replaced by the uranyl UO_2—*i.e.* as $H(UO_2)PO_4$. This salt is formed as a hydrated gelatinous yellow precipitate, on mixing a solution of uranyl nitrate with disodium phosphate. The precipitation occurs in the presence of acetic acid, but not in the presence of hydrochloric acid. If, moreover, there be present an excess of an ammonium salt, the ammonia enters into the composition of the bright yellow gelatinous precipitate formed, in the proportion $UO_2NH_4PO_4$ (with water). This precipitate is not soluble in water and acetic acid, and its solution in inorganic acids when boiled entirely expels all the phosphoric acid. This fact is taken

Uranium, which gives an oxide, UO_3, and the corresponding salt UO_2X_2 and dioxide UO_2, to which the salts UX_4 correspond, is rarely met with in nature. Uranite or the double orthophosphate of uranic oxide, $R(UO_2)H_2P_2O_8,7H_2O$, where R=Cu or Ca, uranium-vitriol $U(SO_4)_2,H_2O$, samarakite, and æschynite, are very rarely found, and then only in small quantities. Of more frequent and abundant occurrence is the non-crystalline, earthy brown uranium ore known as *pitchblende* (sp. gr. 7·2), which is mainly composed of the intermediate oxide $U_3O_8=UO_2,2UO_3$. This ore is found at Joachimsthal in Bohemia in the Erzgebirge, from which the greater part of the uranium used is exported. This ore contains a number of different impurities, chiefly sulphides and arsenides of lead and iron, as well as lime and silica compounds. It is roasted in order to expel the arsenic and sulphur, ground, washed with dilute hydrochloric acid, which does not dissolve the uranoso-uranic oxide, U_3O_8, and the residue is dissolved in nitric acid, which transforms the uranium oxide into the nitrate, $UO_2(NO_3)_2$.

It must be observed that the oxide of uranium, first distinguished by Klaproth (1789), was for a long time regarded as able to give metallic uranium under the action of charcoal and other reducing agents (with the aid of heat). But the substance thus obtained was only the *uranium dioxide*, UO_2. The compound nature of this dioxide,[12] or the presence of oxygen in it, was demonstrated by Peligot (1841), by igniting it with charcoal in a stream of chlorine. He thus obtained a volatile *uranium tetrachloride*, UCl_4,[13] which, when heated with sodium,

advantage of for removing phosphoric acid from solutions—for instance, from those containing salts of calcium and magnesium.

[12] Uranium dioxide, or *uranyl*, UO_2, which is contained in the salts UO_2X_2, has the appearance and many of the properties of a metal. Uranic oxide may be regarded as uranyl oxide, $(UO_2)O$, its salts as salts of this uranyl; its hydroxide, $(UO_2)H_2O_2$, is formed like CaH_2O_2. The green oxide of uranium, uranoso-uranic oxide (easily formed from uranic salts by the loss of oxygen), $U_3O_8=UO_2,2UO_3$, when ignited with charcoal or hydrogen (dry) gives a brilliant crystalline substance of sp. gr. about 10·0, whose appearance resembles that of metals, and which decomposes steam at a red heat with the evolution of hydrogen, but which, however, does not decompose hydrochloric or sulphuric acid, but is oxidised by nitric acid. The same substance is also obtained by igniting the compound $(UO_2)K_2Cl_4$ in a stream of hydrogen, according to the equation $UO_2K_2Cl_4+H_2=UO_2+2HCl+2KCl$. It was at first regarded as the metal. In 1841 Peligot found that it contained oxygen, because carbonic oxide and anhydride were evolved when it was ignited with charcoal in a stream of chlorine, and from 408 parts of the substance which was considered to be metal he obtained 873 parts of a volatile product containing 213 parts of chlorine. From this it was concluded that the substance taken contained an equivalent amount of oxygen. As 213 parts of chlorine correspond with 48 parts of oxygen, it followed that 408−48=360 parts of metal were combined in the substance considered as such with 48 parts of oxygen, and also in the chlorine compound obtained with 213 parts of chlorine.

[13] *Uranium tetrachloride*, uranous chloride, UCl_4, corresponds with uranous oxide as a base. It was obtained by Peligot by igniting uranic oxide mixed with charcoal in a stream of *dry* chlorine: $UO_3+3C+2Cl_2=UCl_4+3CO$. This green volatile compound

gave *metallic uranium* as a grey metal, having a specific gravity of 18·7, and liberating hydrogen from acids, with the formation of green uranous salts, UX_4, which act as powerful reducing agents.[14]

(Note 12) crystallises in regular octahedra, is very hygroscopic, easily soluble in water, with the development of a considerable amount of heat, and no longer separates out from its solution in an anhydrous state, but disengages hydrochloric acid when evaporated. The solution of uranous chloride in water is green. It is also formed by the action of zinc and copper (forming cuprous chloride) on a solution of uranyl chloride, UO_2Cl_2, especially in the presence of hydrochloric acid and sal-ammoniac. Solutions of uranyl salts are converted into uranous salts by the action of various reducing agents, and among others by organic substances or by the action of light, whilst the salts UX_4 are converted into uranyl salts, UO_2X_2, by exposure to air or by oxidising agents. Solutions of the green uranyl salts act as powerful reducing agents, and give a brown precipitate of the uranous hydroxide, UH_4O_4, with potash and other alkalis. This hydroxide is easily soluble in acids but not in alkalis. On ignition it does not form the oxide UO_2, because it decomposes water, but when the higher oxides of uranium are ignited in a stream of hydrogen or with charcoal they yield uranous oxide. Both it and the chloride UCl_4 dissolve in strong sulphuric acid, forming a green salt, $U(SO_4)_2,2H_2O$. The same salt, together with uranyl sulphate, $UO_2(SO_4)$, is formed when the green oxide U_3O_8 is dissolved in hot sulphuric acid. The salts obtained in the latter instance may be separated by adding alcohol to the solution, which is left exposed to the light; the alcohol reduces the uranyl salt to uranous salt, an excess of acid being required. This salt is remarkable from the fact that an excess of water decomposes it, forming a basic salt, which is also easily produced under other circumstances, and contains $UO(SO_4),2H_2O$ (which corresponds to the uranic salt).

[14] It must be observed that the atomic weight of uranium was formerly taken as half the present one. Thus, according to Peligot, U = 120, and the oxide U_2O_3, suboxide UO, and green oxide U_3O_4, were of the same types as the oxides of iron. With a certain resemblance to the elements of the iron group, uranium presents many points of distinction which do not permit its being grouped with them. Thus uranium forms a very stable oxide, U_2O_3(U = 120), but does not give the corresponding chloride U_2Cl_6 (Roscoe, however, in 1874 obtained UCl_5, like $MoCl_5$ and WCl_5), and under those circumstances (the ignition of oxide of uranium mixed with charcoal, in a stream of chlorine), when the formation of this compound might be expected, it gives (U = 120) the chloride UCl_2, which is characterised by its volatility, which is not a property, to such an extent, of any of the dichlorides, RCl_2, of the iron group.

The alteration or doubling of the atomic weight of uranium—*i.e.* the recognition of U = 240—was made for the first time in the first (Russian) edition of this work (1871), and in my memoir (of the same year in Liebig's *Annalen*), because with an atomic weight 120, uranium could not be placed in the periodic system. I think it will not be superfluous to add the following remarks on this subject: (1) In the other groups (K—Rb—Cs, Ca—Sr—Ba, Cl—Br—I) the acid character of the oxides decreases and their basic character increases with the rise of atomic weight, and therefore we should expect to find the same in the group Cr—Mo—W—U, and if CrO_3, MoO_3, WO_3 be the anhydrides of acids, then we indeed find a decrease in their acid character, and therefore uranium trioxide, UO_3, should be a very feeble anhydride, but its basic properties should also be very feeble. Uranic oxide does indeed show these properties, as was pointed out above (Note 10). (2) Chromium and its analogues, besides the oxides RO_3, also form lower grades of oxidation RO_2, R_2O_3, and the same is seen in uranium; it forms UO_3, UO_2, U_2O_5 and their compounds. (3) Molybdenum and tungsten, in being reduced from RO_3, easily and frequently give an intermediate oxide of a blue colour, and uranium shows the same property; giving the so-called green oxide which, according to existent researches, must be regarded as $U_3O_8 = UO_2,2UO_3$, analogous to Mo_3O_8. (4) The higher chlorides, RCl_6, possible for the elements of this group, are either unstable (WCl_6) or do not exist at all

As the salts of uranic oxide are reduced in the absence of organic matter by the action of light, and as they impart a characteristic coloration to glass,[15] they find a certain application in photography and glass work.

If we compare together the highly acid elements, sulphur, selenium, and tellurium, of the uneven series of the sixth group with chromium, molybdenum, tungsten, and uranium of the even series of the same group, we find that the resemblance of the higher form RO_3 does not extend to the lower forms, and even entirely disappears in the elements, because there is not the smallest resemblance between sulphur and chromium and their analogues in a free state. In other words, this means that the small periods, like Na, Mg, Al, Si, P, S, Cl, containing seven elements, do not contain any near analogues of chromium, molybdenum, &c., and therefore their true position among the other elements must be looked for only in those large periods which contain two small periods, and whose type is seen in the period containing:

(Cr); but there is one single lower volatile compound, which is decomposed by water, and liable to further reduction into a non-volatile chlorine product and the metal. The same is observed in uranium, which forms an easily volatile chloride, UCl_4, decomposed by water. (5) The atomic volumes, Cr = 8, Mo = 8·6, W = 9·6, and U = 13, are subject to the rule observed in the other similar series, K—Rb, Ca—Sr—Ba, &c., where the atomic volume increases with the atomic weight, and therefore the high sp. gr. of uranium (18·4) is explained by this fact. (6) For uranium, as for chromium and tungsten, yellow tints predominate in the form RO_3, whilst the lower forms are green and blue. (7) Zimmermann (1881) determined the vapour densities of uranous bromide, UBr_4, and chloride, UCl_4, and they (19·4 and 13·2) were found to correspond to the formulæ given above—that is, they confirmed the accepted atomic weight U = 240. Roscoe, a great authority on the metals of this group, was the first to recognise the proposed atomic weight of uranium U = 240, which since Zimmermann's work has been generally recognised.

[15] Uranium glass, obtained by the addition of the yellow salt $K_2U_2O_7$ to glass, has a green-yellow fluorescence, and is sometimes employed for ornaments; it absorbs the violet rays, like the other salts of uranic oxide—that is, it possesses an absorption spectrum in which the violet rays are absent. The index of refraction of the absorbed rays is altered, and they are given out again as greenish-yellow rays; hence, compounds of uranic acid, when placed in the violet portion of the spectrum, emit a greenish-yellow light, and this forms one of the best examples (another is found in a solution of quinine sulphate) of the phenomenon of fluorescence. The rays of light which pass through uranic compounds do not contain the rays which excite the phenomena of fluorescence and of chemical transformation, as the researches of Stokes prove. In thus absorbing the chemical rays, uranic compounds aid the chemical change of substances mixed with them. Hence, uranic compounds are used in photography. Becquerel, Bolton, and Morton have made some most interesting researches on the phosphorescent spectra of the uranium compounds—that is, on the nature of the light emitted by salts of uranium immediately after their exposure to light; these researches show that the bands of light (generally seven, all between C and F of the solar spectrum), and their intersected dark bands suffer a displacement with a change of elements—for example, in the double salts of metals. Concerning the formation of the peroxide form of uranium (Fairley), see Chapter XX. Note 66.

K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br. These periods contain Ca and Zn, giving RO, Sc, and Ga of the third group, Ti and Ge of the fourth and fifth groups, and As of the fifth group, Cr and Se of the sixth group, Mn and Br of the seventh group, and the remaining elements, Fe, Co, Ni, form connective members of the intermediate eighth group, to the description of the representatives of which we shall turn in the following chapters. And now we will proceed to describe *manganese*, Mn=55, as an element of the seventh group of the even series, directly following after Cr=52, and which corresponds with Br=80 to the same degree that Cr does with Se=79. For chromium, selenium, and bromine very close analogues are known, but for manganese as yet none have been obtained—that is, it is the only representative of the even series in the seventh group. In placing manganese with the halogens in one group, the periodic system of the elements only requires that it should bear an analogy to the halogens in the higher type of oxidation—*i.e.* in the salts and acids—whilst it requires that as great a difference should be expected in the lower types and elements as there exists between chromium or molybdenum and sulphur or selenium. And this is actually the case. The elements of the seventh group form a higher salt-forming oxide, R_2O_7, and its corresponding hydrate, HRO_4, and salts—for example, $KClO_4$. Manganese in the form of potassium permanganate, $KMnO_4$, actually presents a perfect analogy to potassium perchlorate, $KClO_4$. The analogy of the crystalline form of both salts was shown by Mitscherlich. The salts of permanganic acid are also nearly all soluble in water, like those of perchloric acid, and if the silver salt of the latter, $AgClO_4$, be sparingly soluble in water, so also is silver permanganate, $AgMnO_4$. The specific volume of potassium perchlorate is equal to 55, because its specific gravity=2·54; the specific volume of potassium permanganate is equal to 58, because its specific gravity=2·71. Both acids in a free state are soluble in water and volatile, both are powerful oxidisers—in a word, their analogy is still closer than that of chromic and sulphuric acids, and those points of distinction which they present also appear among the nearest analogues—for example, in sulphuric and telluric acids, in hydrochloric and hydriodic acids, &c. Besides which, manganese gives a lower grade of oxidation, MnO_3, analogous to sulphuric and chromic trioxides, and with it corresponds potassium manganate, K_2MnO_4, isomorphous with potassium sulphate.[16] In the types of

[16] The comparison of potassium permanganate with potassium perchlorate, or of potassium manganate with potassium sulphate, shows directly that many of the physical and chemical properties of substances do not depend on the nature of the elements,

oxidation of manganese lower than the permanganates there is no longer any resemblance to chlorine, whilst every point of resemblance disappears when we come to the elements themselves—*i.e.* to manganese and chlorine—for manganese is a metal, like iron, which combines directly with chlorine to form a saline compound, $MnCl_2$, analogous to magnesium chloride.[17]

Manganese belongs to the number of metals widely distributed in nature, especially in those localities where iron occurs, whose ores frequently contain compounds of manganous oxide, MnO, which presents a resemblance to ferrous oxide, FeO, and to magnesia. In many minerals, magnesia and the oxides allied to it are replaced by manganous oxide. Calc spars and magnesites—*i.e.* $R''CO_3$ in general—are frequently met with containing manganous carbonate, which also occurs in a separate state, although but rarely. The soil and the ash of plants generally contain a small quantity of manganese. In the analysis of minerals it is generally found that manganese occurs together with magnesia, because, like it, manganous oxide remains in solution in the presence of ammoniacal salts, not being precipitated by reagents. The property of this manganous oxide, MnO, of passing into the higher grades of oxidation under the influence of heat, alkalis, and air, gives an easy means not only of discovering the presence of manganese in admixture with magnesia, but also of separating these two analogous bases. Magnesia is not able to give higher grades of oxidation, whilst manganese gives them with great facility. Thus, for instance, an *alkaline* solution of sodium hypochlorite produces a precipitate of manganese dioxide in a solution of a manganous salt: $MnCl_2 + NaClO + 2NaHO = MnO_2 + H_2O + 3NaCl$; whilst magnesia is not changed under these circumstances. If the magnesia be precipitated owing to the presence of alkali, it may be dissolved *in acetic acid*, in which manganese dioxide is insoluble. The presence of small quantities of manganese may also be recognised by the green coloration which alkalis acquire when heated with manganese compounds in the air. This green coloration depends on the property of manganese of giving a green alkaline manganate: $MnCl_2 + 4KHO + O_2 = K_2MnO_4 + 2KCl + 2H_2O$. This *faculty of oxidising in the presence of alkalis* forms an essential character of manganese. Therefore manganese often occurs in nature as the different higher oxides. However, the ores of manganese are not so

but on the atomic types in which they appear, on the kind of movements, or on the positions in which the atoms forming the molecule occur.

[17] If, however, we compare the spectra (Vol. I. p. 556) of chlorine, bromine, and iodine with that of manganese one cannot but remark a certain resemblance or analogy which connects manganese both to iron and to chlorine, bromine, and iodine.

very widely distributed in nature, although the manganous compounds are met with nearly everywhere. The most important ore of manganese is its dioxide, or so-called *peroxide*, MnO_2, which is known in mineralogy as *pyrolusite*. Then, manganese occurs as an oxide corresponding with magnetic iron ore, $MnO,Mn_2O_3=Mn_3O_4$, forming the mineral known as *hausmannite*. The oxide Mn_2O_3 also occurs in nature as the anhydrous mineral *braunite*, and in a hydrated form, Mn_2O_3,H_2O, called *manganite*. Both of these often occur as an admixture in pyrolusite. Besides which, manganese is met with in nature as *rhodonite*, or silicate, $MnSiO_3$. Very fine and rich deposits of manganese ores have been found in the Caucasus, the Urals, and along the Dnieper. Those at the Sharapansky district of the Government of Kutais and at Nicopol on the Dnieper are particularly rich. A large quantity of the ore (up to 65000 tons yearly) from these localities is exported.

Manganese gives oxides of the following forms: MnO, manganous oxide, and manganous salts, MnX_2, corresponding with the base, which resembles magnesia and ferrous oxide in many respects; Mn_2O_3, a very feeble base, giving salts, MnX_3, analogous to the aluminium and ferric salts; MnO_2, dioxide, generally called peroxide, an almost indifferent oxide, although feebly acid;[18] MnO_3, manganic anhydride, which forms salts resembling potassium sulphate; Mn_2O_7, permanganic anhydride, giving salts analogous to the perchlorates.

All the oxides of manganese when heated with acids give salts, M_nX_2, corresponding with the lower grade of oxidation, *manganous oxide*, MnO. Manganic oxide, Mn_2O_3, is a feebly energetic base; it is true that it dissolves in hydrochloric acid and gives a dark solution containing the salt $MnCl_3$, but the latter when heated evolves chlorine and gives a salt corresponding with manganous oxide—*i.e.* at first: $Mn_2O_3+6HCl=3H_2O+Mn_2Cl_6$, and then the Mn_2Cl_6 decomposes into $2MnCl_2+Cl_2$. In this manner none of the higher grades of oxidation have a basic character, but *act as oxidising agents in the presence of acids*, disengaging oxygen and passing into salts of the lower grade of oxidation of manganese, MnO. Owing to this circumstance, *the manganous salts* are easily obtained, and they are generally left in

[18] The name 'peroxide' should only be retained for those *highest* oxides (and MnO_2 stands between MnO and MnO_3) which by a direct method of double decomposition are able to either give hydrogen peroxide or contain a larger proportion of oxygen than the base or the acid (the lower oxides), just as hydrogen peroxide contains more oxygen than water. Their type will be H_2O_2, and they are exemplified by barium peroxide, BaO_2, and sulphur peroxide, S_2O_7, &c. Such a dioxide as MnO_2 is, in all probability, a salt—that is, a manganous manganate, MnO_3MnO, and also, as a basic salt of a feeble base, capable of combining with alkalis and acids. Therefore the name of manganese peroxide should be abandoned, and replaced by manganese dioxide. PbO_2 is better termed lead dioxide than peroxide.

the residual solution from the application of the peroxide for the preparation of oxygen and chlorine.[19]

[19] For the preparation of oxygen, manganese dioxide is heated with sulphuric acid: $MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$; or else the dioxide is heated alone to a high temperature, when it gives the intermediate oxide $3MnO_2 = Mn_3O_4 + O_2$; when heated with sulphuric acid this also gives manganous sulphate and oxygen. For the preparation of chlorine the dioxide is heated with hydrochloric acid, and manganese chloride, $MnCl_2$, is obtained in the residue. These two manganous salts may be taken as examples of the derivative of manganous oxide, MnO. Manganous sulphate generally contains various impurities, from the majority of which it may be separated by crystallisation; but it generally contains a large amount of iron salts, from which it cannot be freed in this manner. Their removal may, however, be effected by mixing a portion of the liquid with a solution of sodium carbonate; double decomposition then ensues in this portion, and a precipitate of manganous carbonate is formed. This precipitate is collected and washed, and then added to the remaining mass of the impure solution of manganous sulphate; on heating the solution with this precipitate, the whole of the iron is precipitated as oxide. This is due to the fact that in the solution of the manganese dioxide in sulphuric acid the whole of the iron is converted into the ferric state (because the peroxide acts as an oxidising agent), which, as an exceedingly feebly energetic base precipitated by calcium carbonate and other kindred salts, is also precipitated by manganous carbonate. After being treated in this manner, the solution of manganous sulphate is obtained pure. If it be a bright red colour it is due to the presence of higher grades of oxidation of manganese; they may be destroyed by boiling the solution, when the oxygen from the oxides of manganese is evolved and the manganous salt is obtained. This salt is remarkable for the facility with which it gives various combinations with water. By evaporating the almost colourless solution of *manganous sulphate* at very low temperatures, and by cooling the saturated solution at about 0°, crystals are obtained containing 7 atoms of water of crystallisation, $MnSO_4,7H_2O$, which are isomorphous with cobaltous and ferrous sulphates. These crystals, even at 10°, lose 5 p.c. of water, and completely effloresce at 15°, losing about 20 p.c. of water. By evaporating a solution of the salt at the ordinary temperature, but not above 20°, crystals are obtained containing 5 mol. H_2O, which are isomorphous with copper sulphate; whilst if the crystallisation be carried on between 20° and 30°, large transparent prismatic crystals are formed containing 4 mol. H_2O (see Nickel). A boiling solution also deposits these crystals together with crystals containing 3 mol. H_2O, whilst the first salt, when fused and boiled with alcohol, gives crystals containing 2 mol. H_2O. Graham obtained a monohydrated salt by drying the salt at about 200°. The last atom of water is eliminated with difficulty, as is the case with all salts isomorphous with magnesium sulphate. The crystals containing a considerable amount of water are rose-coloured, and the anhydrous crystals are colourless. The solubility of manganous sulphate is given in Vol. I. p. 71, Note 24, whence it is seen that at the boiling-point this salt is much less soluble than at lower temperatures, and therefore a solution saturated at the ordinary temperature becomes turbid when boiled. Manganous sulphate, being analogous to magnesium sulphate, is decomposed, like the latter, when ignited, but it does not then leave manganous oxide, but the intermediate oxide, Mn_3O_4. It gives double salts with the alkali sulphates. It is also remarkable that with aluminium sulphate it forms fine radiated crystals whose composition resembles that of the alums—namely, $MnAl_2(SO_4)_4,24H_2O$. This salt is easily soluble in water, and occurs in nature.

Manganous chloride crystallises with 4 mol. H_2O, like the ferrous salt, and not with 6 mol. H_2O like many kindred salts—for example, those of cobalt, calcium, and magnesium; 100 parts of water dissolve 88 parts of the anhydrous salt at 10° and 55 parts at 62°. Alcohol also dissolves manganous chloride, and the alcoholic solution burns with a red flame. This salt, like magnesium chloride, readily forms double salts. Potassium cyanide with manganous salts produces a yellowish-grey precipitate, MnC_2N_2, soluble in an excess of the reagent, a double salt, $K_4MnC_6N_6$, corresponding with potassium ferro-

The fact alone that the oxides of manganese are not reduced to metal when ignited in hydrogen (whilst the oxides of iron give metallic

cyanide, being formed. On evaporation of this solution a portion of the manganese is oxidised and precipitated, whilst a salt corresponding to Gmelin's red salt, $K_3MnC_6N_6$, remains in solution. Sulphuretted hydrogen does not precipitate the salts of manganese, not even the acetate, but ammonium sulphide gives a flesh-coloured precipitate. Oxalic acid in strong solutions of manganous salts gives a white precipitate of the oxalate, MnC_2O_4. This precipitate is insoluble in water, and is used for the preparation of manganous oxide itself because it decomposes when ignited, with the formation of carbonic anhydride, carbonic oxide, and manganous oxide. *Manganous oxide* thus obtained is a green powder, which, however, oxidises with such facility that it burns in air when brought into contact with an incandescent substance, and passes into the red intermediate oxide Mn_3O_4; so that the above experiment must be carried on in a tube without access of air. In solutions of manganous salts, alkalis produce a precipitate of the hydroxide MnH_2O_2, which rapidly absorbs oxygen in the presence of air, and gives the brown intermediate oxide, or, more correctly speaking, its hydrate.

Manganous oxide, besides being obtained by the above-described method from manganous oxalate, may also be obtained by igniting the higher oxides in a stream of hydrogen and also from manganese carbonate. The manganous oxide ignited in the presence of hydrogen acquires a great density, and is no longer so easily oxidised. It may also be obtained in a crystalline form, if during the ignition of the carbonate or higher oxide a trace of dry hydrochloric acid gas be passed into the stream of hydrogen. It is thus obtained in the form of transparent emerald green crystals of the regular system; but in this state it is easily soluble in acids.

Manganous oxides in oxidising give the *red oxide of manganese*, Mn_3O_4. This is the most stable of all the oxides of manganese; it is not only stable at the ordinary but also at a high temperature—that is, it does not absorb or disengage oxygen by itself. When ignited, all the higher oxides of manganese pass into it by losing oxygen, and manganous oxide by absorbing oxygen. This oxide does not give any independent salts, but it dissolves in sulphuric acid, forming a dark red solution, which contains both manganous and manganic (of the *oxide*, Mn_2O_3) sulphates. The latter with potassium sulphate gives a manganese alum, in which the alumina is replaced by its isomorphous oxide of manganese. But this alum, like the solution of the intermediate oxide in sulphuric acid, evolves oxygen and leaves a manganous salt, when slightly heated.

Manganese dioxide is still less basic than the oxide, and disengages oxygen or a halogen in the presence of acids, forming manganous salts, like the oxide. However, if it be placed in ether, and hydrochloric acid gas passed into the mixture, which is kept cool, then the ether acquires a green colour, owing to the formation of a compound, $MnCl_4$, corresponding with the dioxide which passes into solution. It is, however, very unstable and exceedingly easily decomposed, with the evolution of chlorine. The corresponding fluoride obtained by Nicklés is much more stable. At all events, manganese dioxide does not exhibit any well-defined basic character, but is rather of an acid character, which is particularly shown in the compounds MnF_4 and $MnCl_4$ just mentioned, and in the property of dioxide of manganese of combining with alkalis. If the higher grades of oxidation of manganese be deoxidised in the presence of alkalis, they frequently give the dioxide combined with the alkali—for example, in the presence of potash a compound is formed which contains $K_2O,5MnO_2$, which shows the feeble acid character of this oxide. When ignited in the presence of sodium compounds, manganese dioxide frequently forms the compound $Na_2O,12MnO_2$ (Rousseau). In general, manganese dioxide has the character of an exceedingly feebly energetic intermediate oxide; perhaps it is a saline compound containing $MnOMnO_3$ or $(MnO)_3Mn_2O_7$, but there is no firm basis for such a supposition, although it is known that manganous chloride and potassium permanganate give the dioxide in the presence of alkalis.

Manganese dioxide may be obtained from manganous salts by the action of oxidising agents. If manganous hydroxide or carbonate be shaken up in water through which

iron under these circumstances), but only to manganous oxide, MnO, shows that manganese has a considerable affinity for oxygen—that is, is difficult to reduce. This may be done, however, by means of charcoal or sodium at a very high temperature. A mixture of one of the oxides of manganese with charcoal or organic matter gives fused *metallic manganese* under the powerful heat developed by coke with an artificial draught. The metal was obtained for the first time in this manner by Gahn, after Pott, and more especially Scheele, had in the last century shown the difference between the compounds of iron and manganese (they were previously regarded as being the same). Manganese is prepared by mixing one of its oxides in a finely-divided state with oil and soot; the resultant mass is then first ignited in order to decompose the organic matter, and then strongly heated in a charcoal crucible. The manganese thus obtained, however, contains, as a rule, a considerable amount of silicon and other impurities. Its specific gravity is stated as varying from 7·2 to 8·0. It has a light grey colour, a feebly metallic lustre, and although it is very hard it is acted on by a file. It rapidly oxidises in air, being converted into a black oxide; water acts on it at the ordinary temperature, with the evolution of hydrogen, and this decomposition proceeds very rapidly with boiling water.[20]

chlorine is passed, then manganese hypochlorite is not formed, as is the case with certain other oxides, but manganese dioxide is precipitated: $2MnO_2H_2 + Cl_2 = MnCl_2 + MnO_2,H_2O + H_2O$. Owing to this fact, hypochlorites in the presence of alkalis and acetic acid when added to a solution of manganous salts give hydrated manganese dioxide, as was mentioned above. Manganous nitrate also leaves manganese dioxide when heated to 200°. It is also obtained from manganous and manganic salts of the alkalis, when they are decomposed in the presence of a small amount of acid; the practical method of converting the salts MnX_2 into the higher grades of oxidation is given in Chapter II. Note 6.

[20] Other chemists have obtained manganese by different methods, and attributed different properties to it. This difference probably depends on the impurities which are dissolved during the smelting of the manganese. It is very possible, and even very probable, that, besides silicon, manganese is able to dissolve carbon—that is, to form a compound with it something like cast iron—and this reason may account for variations in its properties. Deville obtained manganese by subjecting the pure dioxide, mixed with pure charcoal (from burnt sugar), to a strong heat in a lime crucible until the resultant metal fused. The metal obtained had a rose tint, like bismuth, and like it was very brittle, although exceedingly hard. It decomposed water at the ordinary temperature. Brunner obtained manganese having a specific gravity of about 7·2, which decomposed water very feebly at the ordinary temperature, did not oxidise in air, and was capable of taking a bright polish, like steel; it had the grey colour of cast iron, was very brittle, and hard enough to scratch steel and glass, like a diamond. Brunner's method was as follows. He decomposed the manganese fluoride (obtained as a soluble compound by the action of hydrofluoric acid on manganese carbonate) with sodium, by mixing these substances together in a crucible and covering the mixture with a layer of salt and fluor spar; after which the crucible was first gradually heated until the reaction began, and then strongly heated in order to fuse the metal separated. At all events, manganese is a metal which decomposes water more easily than iron, nickel, and cobalt.

If manganese dioxide, or any lower oxide of manganese, be heated with an alkali in the presence of air, the mixture absorbs oxygen from the air,[21] and forms an alkaline manganate of a green colour: $2KHO + MnO_2 + O = K_2MnO_4 + H_2O$. Steam is disengaged during the ignition of the mixture, and if this does not take place there is no absorption of oxygen. The oxidation proceeds much more rapidly if, before igniting in air, potassium chlorate or nitre be added to the mixture, and this is the usual method of preparing *potassium manganate*, K_2MnO_4. The resultant mass dissolved in a small quantity of water gives a dark green solution, which, when evaporated under the receiver of an air-pump over sulphuric acid, deposits green crystals of exactly the same form as potassium sulphate—namely, six-sided prisms and pyramids. The composition of the crystals is not changed by being redissolved, if perfectly pure water free from air and carbonic acid be taken. But in the presence of even very feeble acids the solution of this salt changes its colour and becomes red, and deposits manganese dioxide. The same decomposition takes place when the salt is heated with water, but when diluted with a large quantity of unboiled water the manganese dioxide is not separated, although the solution turns red. This change of colour depends on the fact that potassium manganate, whose solution is green, is transformed into potassium permanganate, whose solution is of a red colour. The reaction proceeding under the influence of acids and a large quantity of water is expressed in the following manner: $3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KHO$. When there is a small quantity of free acid it combines with the liberated alkali. If there is a large proportion of acid and the decomposition is aided by heat, then the manganese dioxide and potassium permanganate are also decomposed, with formation of manganous salt. Exactly the same decomposition as takes place under the action of acids is also accomplished by magnesium sulphate, which reacts in many cases like an acid. When water holding atmospheric oxygen in solution acts on a solution of potassium manganate, then the oxygen combines directly with the manganate and forms potassium permanganate, without precipitating dioxide of manganese: $2K_2MnO_4 + O + H_2O = 2KMnO_4 + 2KHO$. Thus a solution of potassium manganate undergoes a very characteristic change in colour and passes from green to red under exceedingly slight agencies; hence this salt received the name of *chameleon mineral*.[22]

[21] Vol. I. p. 157, Note 7.

[22] It was known by this name to the alchemists, but the true explanation of the change in colour is due to the researches of Chevillot, Edwards, Mitscherlich, and Forchhammer. The change in colour of potassium manganate is due to its insta-

Potassium permanganate, $KMnO_4$, crystallises in well-formed, long red prisms with a bright green metallic lustre. In the arts the potash is frequently replaced by soda, and even by other alkaline bases, but no salt of permanganic acid crystallises so well as the potassium salt, and therefore this salt is exclusively used in chemical laboratories. One part of the crystalline salt dissolves in 15 parts of water at the ordinary temperature. The solution is of a very deep *red colour*, which is so intense that it is still clearly observable after being highly diluted with water. The decompositions to which this salt is liable in many cases are very remarkable. In a solid state it is decomposed by heat, with evolution of oxygen, a residue consisting of the red oxide of manganese and potassium oxide being left. The solution of this salt with an excess of impure commercial alkali generally acquires a green tint. The reason of this change in colour must be ascribed to the fact that a manganate is formed, and a portion of the oxygen thus liberated passes over to the organic matter mixed in the impure alkali, because pure solutions of alkalis do not produce a change in colour even when boiled and evaporated. A number of substances reduce potassium permanganate to manganese dioxide; many organic substances (although far from all, even when boiled in a solution of permanganate) act in this manner, being oxidised at the expense of a portion of the oxygen of the permanganate. Thus, a solution of sugar decomposes a cold solution of potassium permanganate. In the presence of an excess of alkali, with a small quantity of sugar, the reduction leads to the formation of potassium manganate, because $2KMnO_4 + 2KHO = O + 2K_2MnO_4 + H_2O$.

bility and to its splitting up into two other manganese compounds, a higher and a lower: $3MnO_3 = Mn_2O_7 + MnO_2$. Manganese trioxide is really decomposed in this manner by the action of water (see later): $3MnO_3 + H_2O = 2MnHO_4 + MnO_2$ (Franke, Thorpe, and Hambly). The instability of the salt is proved by the fact of its being deoxidised by organic matter, with the formation of manganese dioxide and alkali, so that, for instance, a solution of this salt cannot be filtered through paper. The presence of an excess of alkali increases the stability of the salt; when heated it breaks up in the presence of water, with the evolution of oxygen.

The mode of preparing *potassium permanganate* will be understood from the above. There are many receipts for preparing this substance, as it is now used in considerable quantities both for technical and laboratory purposes. But in all cases the essence of the methods is one and the same: a mixture of alkali with any oxide of manganese (even manganous hydroxide, which may be obtained from manganous chloride) is first heated in the presence of air or of an oxidising substance (for the sake of quickness, with potassium chlorate); the resultant mass is then treated with water and heated, when manganese dioxide is precipitated and potassium permanganate remains in solution. This solution may be boiled, as the liquid will contain free alkali; but the solution cannot be evaporated to dryness, because a strong solution, as well as the solid salt, is decomposed by heat.

By adding a dilute solution of manganous sulphate to a boiling mixture of lead dioxide and dilute nitric acid, the whole of the manganese may be converted into permanganic acid (Crum).

With a considerable amount of sugar and a more prolonged action, the solution turns brown and precipitates manganese dioxide or even oxide. When a solution of potassium permanganate mixed with alkali is shaken up with a large quantity of many organic substances, the oxidation is generally accompanied by the evolution of heat and precipitation of manganese dioxide. In this case three-eighths of the oxygen in the salt are utilised for oxidation: $2KMnO_4 = K_2O + 2MnO_2 + O_3$. A portion of the alkali liberated is retained by the manganese dioxide, and the other portion generally combines with the substance oxidised, because the latter most frequently gives an acid with an excess of alkali. A solution of potassium iodide acts in a similar manner, being converted into potassium iodate at the expense of the three atoms of oxygen disengaged by two molecules of potassium permanganate. A mixture of crystallised potassium permanganate and phosphorus or sulphur takes fire when rubbed or struck; a mixture with charcoal only burns when heated and not when struck. The instability of the salt is also seen from the fact that its solution is decomposed by hydrogen peroxide.[23]

In the presence of acids potassium manganate acts as an oxidising agent with still greater energy than in the presence of alkalis. At all events, a greater proportion of oxygen is then available for oxidation, namely, not $\frac{3}{8}$, as in the presence of alkalis, but $\frac{5}{8}$, because in the first instance manganese dioxide is formed, and in the second case manganous oxide, or rather the salt, MnX_2, corresponding with it. Thus, for instance, in the presence of an excess of sulphuric acid, the decomposition is accomplished in the following manner: $2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$. This decomposition, however, does not proceed directly on mixing a solution of the salt with sulphuric acid, and crystals of the salt even dissolve in oil of vitriol without the evolution of oxygen, and this solution only decomposes by degrees after a certain time. This is due to the fact that sulphuric acid liberates free permanganic acid from the permanganate,[24] which acid is

[23] A solution of potassium permanganate gives a beautiful absorption spectrum. If the light in passing through this solution loses a portion of its rays in it (if one may so account for it), this is partially explained by the increased oxidising power which the solution then acquires. We may here also remark that a dilute solution of permanganate of potassium forms a colourless solution with nickel salts, because the green colour of the solution of nickel salts is complementary to the red. Such a decolorised solution, containing a large proportion of nickel and a small proportion of manganese, decomposes after a time, throws down a precipitate, and re-acquires the green colour proper to the nickel salts.

[24] If sulphuric acid is allowed to act on potassium permanganate without any special precautions, a large amount of oxygen is evolved (it may even explode and inflame), and violet spray of the decomposing permanganic acid is jerked up. But if the pure salt (especially free from chlorine) be dissolved in pure well-cooled sulphuric acid, without any rise in temperature, then a green coloured liquid settles at the bottom of the vessel.

stable in solution. But if, in the presence of acids and a permanganate, there is a substance capable of absorbing oxygen—for instance, capable of passing into a higher grade of oxidation—then the reduction of the permanganic acid into manganous oxides sometimes proceeds directly on mixing. This reduction is very clearly seen, because the solutions of potassium permanganate are red whilst the manganous salts are

This liquid does not contain any sulphuric acid, and consists of permanganic anhydride, Mn_2O_7 (Aschoff, Terreil). It is impossible to prepare any considerable quantity of the anhydride by this method, as it decomposes with an explosion as it collects, evolving oxygen and leaving red oxide of manganese. *Permanganic anhydride*, Mn_2O_7, in dissolving in sulphuric acid, gives a green solution, which (according to Franke, 1887) contains a compound $Mn_2SO_{10}=(MnO_3)_2SO_4$—that is, sulphuric acid in which both hydrogens are replaced by the group MnO_3, which is combined with OK in permanganate of potassium. This mixture with a small quantity of water gives Mn_2O_7, according to the equation: $(MnO_3)_2SO_4+H_2O=H_2SO_4+Mn_2O_7$, and when heated to 30° it gives *manganese trioxide*, $(MnO_3)_2SO_4+H_2O=2MnO_3+H_2SO_4+O$. Pure manganese trioxide is obtained if the solution of $(MnO_3)_2SO_4$ be poured in drops on sodium carbonate. Then, together with carbonic anhydride, there flies over a spray of manganese trioxide, which may be collected in a well-cooled receiver, and this shows that the reaction proceeds according to the equation: $(MnO_3)_2SO_4+Na_2CO_3=Na_2SO_4+2MnO_3+CO_2+O$ (Thorpe). The trioxide is decomposed by water, forming manganese dioxide and a solution of *permanganic acid*: $3MnO_3+H_2O=MnO_2+2HMnO_4$. The same acid is obtained by dissolving permanganic anhydride in water.

Barium permanganate when treated with sulphuric acid gives the same acid. This barium salt may be prepared by the action of barium chloride on the difficultly soluble silver permanganate, $AgMnO_4$, which is precipitated on mixing a strong solution of the potassium salt with silver nitrate. The solution of permanganic acid forms a bright red liquid which reflects a dark violet tint. A dilute solution has exactly the same colour as that of the potassium salt. It deposits manganese dioxide when exposed to the action of light, and also when heated above 60°, and this proceeds the more rapidly the more diluted the solution. It shows its oxidising properties in many cases, as has already been said above. Even hydrogen gas is absorbed by a solution of permanganic acid; and charcoal and sulphur are also oxidised by it, as they are by potassium permanganate. This may be taken advantage of in analysing gunpowder, because when it is treated with a solution of potassium permanganate, all the sulphur is converted into sulphuric acid and all the charcoal into carbonic anhydride. Finely-divided platinum immediately decomposes permanganic acid. With potassium iodide it liberates iodine (which may afterwards be oxidised into iodic acid) (Mitscherlich, Fromhert, Aschoff, and others). Ammonia does not form a corresponding salt with free permanganic acid, because it is oxidised with evolution of nitrogen. The oxidising action of permanganic acid in a strong solution may be accompanied by flame and the formation of violet fumes of permanganic acid; thus a strong solution of it takes fire when brought into contact with paper, alcohol, alkali sulphides, fats, &c.

We will supplement these data respecting permanganic acid with the following disconnected facts:—

According to Franke, 1 part of potassium permanganate with 13 parts of sulphuric acid at 100° gives brown crystals of the salt $Mn_2(SO_4)_3,H_2SO_4,4H_2O$, which gives a precipitate of hydrated manganese dioxide, $H_2MnO_3=MnO_2H_2O$, when treated with water.

Spring, by precipitating potassium permanganate with sodium sulphite and washing the precipitate by decantation, obtained a soluble colloidal manganese oxide, whose composition was the mean between Mn_2O_5 and MnO_2—namely, $Mn_2O_5,4(MnO_2H_2O)$.

almost colourless. Thus, for instance, nitrous acid and its salts are converted into nitric acid and decolorise the acid solution of the permanganate. Sulphurous anhydride and its salts immediately decolourise potassium permanganate, forming sulphuric acid. Ferrous salts, and in general salts of lower grades of oxidation capable of being oxidised in solution, act in exactly the same manner. Sulphuretted hydrogen is also oxidised into sulphuric acid; even mercury is oxidised at the expense of permanganic acid, and decolorises its solution, being converted into mercuric oxide. These reactions may easily be followed to the end, and therefore, having first determined the amount of active oxygen in one volume of a solution of potassium permanganate, and knowing how many volumes are required to effect a given oxidation, it is easy to determine the amount of a substance which is oxidised in a solution from the amount of permanganate expended (Marguerite's method).

The oxidising action of permanganic acid, like all other chemical reactions, is not accomplished instantaneously, but only by degrees. And, as the course of the reaction is here easily followed by determining the amount of salt unchanged in a sample taken at a given moment,[25] the oxidising reaction of potassium permanganate, in an acid liquid, was employed by Harcourt and Esson (1865) as one of the first cases for the investigation of the laws of the *rate of chemical change*[26] as a

[25] For rapid and accurate determinations of this kind, advantage is taken of those methods of chemical analysis which are known as 'titrations' (volumetric analysis), and consist in measuring the volume of solutions of known strength required for the complete conversion of a given substance. Details respecting the theory and practice of titration, in which potassium permanganate is very frequently employed, must be looked for in works on analytical chemistry.

[26] The measurements of velocity and acceleration in mechanics serve for determining the measure of forces, but in this case the velocities are magnitudes of length or paths passed over in a unit of time. The velocity of chemical change forms a conception of quite another kind. In the first place, the velocities of reactions are magnitudes of the masses which have entered into chemical transformations; in the second place, these velocities can only be relative quantities. Hence the conception of 'velocity' has quite a different meaning in chemistry from what it has in mechanics. Their only common factor is time. If dt be the element of time and dx the quantity of a substance changed in this element of time, then the fraction (or quotient) dx/dt will express the rate of the reaction. The natural conclusion, made both by Harcourt and Esson, and previously to them (1850) by Wilhelmj (who investigated the rate of conversion, or inversion, of sugar in its passage into glucose), consists in admitting that this velocity is proportional to the quantity of substance still unchanged—*i.e.*, that $dx/dt = C(A-x)$, where C is a constant coefficient of proportionality, and where A is the quantity of a substance taken for reaction at the moment when $t=0$ and $x=0$—that is, at the beginning of the experiment, from which the time t and quantity x of substance unchanged is counted. On integrating the preceding equation we obtain $\log(A/A-x)=kt$, where k is a new constant, if we take ordinary (and not natural) logarithms. Hence, knowing A, x, and t for each reaction, we find k, and it proves to be a constant quantity. Thus from the figures cited in the text for the reaction $2KMnO_4+10tC_2H_2O_4+14MnSO_4$, it may be

fact of great importance in chemical mechanics. In their experiments they took oxalic acid, $C_2H_2O_4$, which in oxidising gives carbonic anhydride, and, with an excess of sulphuric acid, the potassium permanganate is converted into manganous sulphate, $MnSO_4$, so that the ultimate oxidation will be expressed by the equation: $5C_2H_2O_4 + 2MnKO_4 + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O$. The influence of the relative amount of sulphuric acid is seen from the annexed table, which gives the measure of reaction p per 100 parts of potassium permanganate, taken four minutes after mixing, using n molecules of sulphuric acid, H_2SO_4, per $2KMnO_4 + 5C_2H_2O_4$:

n =	2	4	6	8	12	16	22
p =	22	36	51	63	77	86	92

It is obvious that the temperature and relative amount of every one of the acting and resulting substances should show its influence on the relative velocity of reaction; thus, for instance, direct experiment showed the influence of the admixture of manganous sulphate, depending on the possibility of the formation of manganese dioxide by the reaction of the manganous oxide on the permanganic acid. When a large proportion of oxalic acid (108 molecules) was taken to a large mass of water and to 2 molecules of permanganate, 14 molecules of manganous sulphate was added, then the quantity x of the potassium permanganate acted on (in percentages of the potassium permanganate taken) in t minutes (at 16°) was as follows:

t =	2	5	8	11	14	44	47	53	61	68
x =	5·2	12·1	18·7	25·1	31·3	68·4	71·7	75·8	79·8	83·0

These figures show that the rate of reaction—that is, the quantity of permanganate changed in one minute—decreases proportionally to the decrease in the amount of unchanged potassium permanganate. In one minute, at the commencement, about 2·6 per cent. of the salt taken had reacted, and after an hour about 0·5 per cent. The same phenomena are observed in every case which has been investigated, and this branch of theoretical or physical chemistry, now studied by many,[27] promises to explain the course of chemical trans-

found that $k = 0·0114$; for example, $t = 44$, $x = 68·4$ (A = 100), whence $kt = 0·5004$ and $k = 0·0114$.

[27] The researches made by Hood, Van't Hoff, Ostwald, Warder, Menschutkin, Konovaloff, and others have a particular significance in this subject. Owing to the comparative novelty of this subject, and the absence of applicable as well as indubitable deductions, I consider it impossible to enter into this province of theoretical chemistry,

formations from a fresh point of view, which is closely allied to the doctrine of affinity, because the rate of reaction, without doubt, is connected with the magnitude of the affinities acting between the reacting substances.

although I am quite confident that its development should lead to very important results, especially in respect to chemical equilibria, because Van't Hoff has already shown that the limit of reaction in reversible reactions is determined by the attainment of equal velocities for the opposite reactions.

CHAPTER XXII

IRON, COBALT, AND NICKEL

JUDGING from their atomic weights, and the composition of the higher oxides, it is easy to form a direct conception of the series of elements comprehending seven groups. Such is, for instance, the typical series Li, Be, B, C, N, O, F, or the third series, Na, Mg, Al, Si, P, S, Cl. It is easy to form an idea of the seven groups, because the seven usual types of oxides from R_2O to R_2O_7 correspond with them (Chapter XV.). The position of the eighth group is quite separate, and is determined by the fact that, as we have already seen, in each group of metals having a greater atomic weight than potassium a distinction ought to be made between the elements of the even and uneven series. The series of even elements, commencing with a strikingly alkaline element (potassium, rubidium, cæsium), together with the uneven series following it, concluding with a haloid (chlorine, bromine, iodine), forms one large period, the properties of whose members repeat themselves in other similar periods. The elements of the eighth group are situated between the elements of the even series and the elements of the uneven series following them. And for this reason elements of the eighth group are found in the middle of each large period. The properties of the elements belonging to it are shown with typical clearness in the case of iron, the well-known representative of this group.

Iron is one of those elements which are not only widely diffused in the crust of the earth, but also throughout the entire universe. Its oxides and their various compounds are found in the most diverse portions of the earth's crust; but here iron is always found combined with some other element. Iron is not found on the earth's surface in a free state, because it easily oxidises under the action of air. It is occasionally found in the native state in meteorites, or aerolites, which fall upon the earth.

Meteoric iron is formed outside the earth.[1] Meteorites are fragments

[1] The composition of meteoric iron is various. It generally contains nickel, phosphorus, carbon, &c. The schreibersite of meteoric stones contains Fe_4Ni_2P.

which are carried round the sun in orbits, and fall upon the earth when coming into proximity with it during their motion in space. The meteoric dust, on passing through the upper parts of the atmosphere, and becoming incandescent from friction with the gases, produces that phenomenon which is familiar under the name of falling stars.[2] Such is the doctrine concerning meteorites, and therefore the fact of their containing rocky (siliceous) matter and metallic iron shows that outside the earth the elements and their aggregation are in some degree the same as upon the earth itself.

The most widely-diffused terrestrial compound of iron is iron bisulphide, FeS_2, or *iron pyrites*. It occurs in formations of both aqueous and igneous origin, and sometimes in enormous masses. It is

[2] Comets and the rings of Saturn ought now to be considered as consisting of an accumulation of such meteoric cosmic particles. Perhaps the part played by these minute bodies scattered throughout space is much more important in the formation of the largest celestial bodies than was hitherto conceived. The investigation of this branch of astronomy, due to Schapparelli, has a bearing on the whole of natural science.

The question arises as to why the iron in meteorites is in a free state, whilst on earth it is in a state of combination. Has not this a tendency to show the great diversity in the conditions of our orb from those of the rest? My answer to this question has been already given in Vol. I. p. 365, Note 57. It is my opinion that inside the earth there is a mass similar in composition to meteorites—that is, containing rocky matter and metallic iron, partly carburetted. In conclusion, I consider it will not be out of place to add the following explanations. According to the theory of the distribution of pressures (see my treatise, *On Barometrical Levelling*, 1876, pages 48 *et seq.*) in an atmosphere of mixed gases, it follows that two gases, whose densities are d and d_1, and whose relative quantities or partial pressures at a certain distance from the centre of attraction are h and h_1, will, when at a greater distance from the centre of attraction, present a different ratio of their masses $x : x_1$—that is, of their partial pressures—which may be found by the equation $d_1(\log h - \log x) = d(\log h_1 - \log x_1)$. If, for instance, $d : d_1 = 2 : 1$, if $h = h_1$ (that is to say, the masses are equal at the lower height) $= 1000$, then when $x = 10$ the magnitude of x_1 will not be 10 (*i.e.*, the mass of a gas at a higher level whose density $= 1$ will not be equal to the mass of a gas whose density $= 2$, as was the case at a lower level), but much greater—namely, $x_1 = 100$—that is, the lighter gas will predominate over a heavier one at a higher level. Therefore, when the whole mass of the earth was in a state of vapour, the substances having a greater vapour density accumulated about the centre (speaking relatively, for instance, with respect to the mass of oxygen alone), and those with a lesser vapour density at the surface. And as the density of vapours depends on the atomic and molecular weights, then those substances which have small atomic and molecular weights ought to accumulate at the surface, and those with high atomic and molecular weights, which are the least volatile and the most difficult to condense, at the centre. Thus it is understood why such light elements as hydrogen, carbon, nitrogen, oxygen, sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, potassium, calcium, and their compounds predominate at the surface and form the earth's crust. There is also now much iron in the sun, as spectrum analysis shows, and therefore it entered into the composition of the earth and other planets, but accumulated at the centre, because the density of its vapour is certainly large and it easily condenses, not being volatile. There was also oxygen about the centre of the earth, but not sufficient to combine with the iron. The greatest amount of oxygen (relatively), as a much lighter element, accumulated at the surface, where we at the present time observe all oxidised compounds and even still a remnant of free oxygen.

a substance having a greyish-yellow colour, with a metallic lustre, a sp. gr. of 5·0, and crystallises in the regular system.

The oxides are the principal ores used for producing metallic iron. The majority of the ores contain ferric oxide, Fe_2O_3, either in a free state or combined with water, or else in combination with ferrous oxide, FeO. The qualities and sorts of iron ores are numerous and various. Ferric oxide in a separate form appears sometimes as crystals of the rhombohedric system, having a metallic lustre and greyish steel colour; they are brittle, and form a red powder, specific gravity about 5·25. Ferric oxide in type of oxidation and properties resembles alumina; it is, however, although with difficulty, soluble in acids even when anhydrous. The crystalline oxide bears the name of *specular iron ore*, but ferric oxide most often occurs in a non-crystalline form, in masses having a red fracture, and is then known as *red hæmatite*. In this form, however, it is rather a rare ore, and is principally found in veins. The hydrates of ferric oxide, ferric hydroxides,[3] are most often found in aqueous or stratified formations, and are known as *brown hæmatites;* they generally have a brown colour, form a yellowish-brown powder, have no metallic lustre, but an earthy appearance. They easily dissolve in acids, and diffuse through other formations, especially clays (for instance, ochre); they sometimes occur in reniform and similar masses, evidently of aqueous origin. Such are, for instance, the so-called bog or lake and peat ores found at the bottom of marshes and lakes, and also under and in peat beds. This ore is formed from water containing ferrous carbonate in solution, which, after absorbing oxygen, deposits ferric hydroxide. In rivers and springs iron is found in solution, through the assistance of carbonic acid, as ferrous carbonate: hence the existence of chalybeate springs containing a considerable amount of ferrous carbonate, $FeCO_3$. This ferrous carbonate, or *siderite*, is either found as a non-crystalline product of evidently aqueous origin, or as a crystalline spar called *spathic iron ore*. In the first shape the reniform deposits of this ore are most remarkable; they are called spherosiderites, and sometimes form whole light strata in the jurassic and carboniferous formations. *Magnetic iron ore*, $Fe_3O_4=FeO,Fe_2O_3$, in virtue of its purity and practical uses, is a very

[3] The hydrated ferric oxide is found in nature in a dual form. It is somewhat rarely met with in the form of a crystalline mineral called *göthite*, whose specific gravity is 4·4 and composition $Fe_2H_2O_4$, or $FeHO_2$—that is, one of oxide of iron to one of water: Fe_2O_3,H_2O; most often found as brown ironstone, forming dense masses of fibrous reniform deposits containing $2Fe_2O_3,3H_2O$—that is, having a composition $Fe_4H_6O_9$. In bog ore and other similar ores we most often find a mixture of this hydrated ferric oxide with clay and other impurities. The specific gravity of such formations is rarely as high as 4·0.

important ore; it is a compound of the ferrous and ferric oxides, it is naturally magnetic, has a specific gravity of 5·1, crystallises in well-formed crystals of the regular system, is with difficulty soluble in acids, and sometimes forms enormous masses, as, for instance, Mount Blagodat in the Ural. However, in most cases—for instance, at Korsak-Mogila (to the north of Berdiansk and Nogaiska, near the Azov Sea), or at Krivoi Rog (to the west of Ekaterinoslav)—the magnetic iron ore is mixed with other iron ores. In the Urals, the Caucasus (not to mention Siberia), and in the districts adjoining the coal basin of the Don, Russia possesses the richest iron ores in the world. To the south of Moscow, in the Governments of Toula and Nijninovgorod, in the Olonetz district, and in the Government of Orloffsky (near Zinovieff in the district of Kromsky), and in many other places, there are likewise abundant supplies of iron ores amongst the deposited aqueous formations; the siderite of Orloffsky, for instance, is distinguished by its great purity.[4]

Iron is also found in the form of various other compounds—for instance, in certain silicates, and also in some phosphates; but these forms are comparatively rare in nature in a pure state, and have not the industrial importance of those natural compounds of iron previously mentioned. In small quantities iron enters into the composition of every kind of *soil* and all rocky formations. As ferrous oxide is isomorphous with magnesia, and ferric oxide with alumina, isomorphous substitution is possible here, and therefore minerals are not unfrequently found in which the quantity of iron considerably varies; such, for instance, are pyroxene, amphibole, certain varieties of mica, &c. Although much iron oxide is deleterious to the growth of vegetation, still plants do not flourish without iron; it enters as an indispensable component into the composition of all higher *organisms*; in the ash of plants we always find more or less of its compounds. It also even enters into the blood, and forms one of the colouring matters in it; 100 parts of the blood of the highest organisms contain about 0·05 of iron.

[4] The ores of iron, similarly to all substances extracted from veins and deposits, are worked according to mining practice by means of vertical, horizontal, or inclined excavations which reach and penetrate the veins and strata containing the ore deposits. The mass of ore excavated is raised to the surface, then sorted either by hand or else in special sorting apparatus (generally acting with water to wash the ore), and is subjected to roasting and other treatment. In every case the ore contains foreign matter. In the extraction of iron, which is one of the cheapest metals, the dressing of an ore is in most cases unprofitable, and only ores rich in metal are worked—namely, those containing at least 20 p.c. It is often profitable to transport rich (as much as 70 p.c. of iron) and pure ores from long distances. The details concerning the working and extraction of metals will be found in special treatises on metallurgy and mining.

The *reduction* of the ores of iron into metallic iron is in principle very simple, because when the oxides of iron are strongly heated with charcoal, hydrogen, carbonic oxide, and other reducing agents,[5] they easily give metallic iron. But the matter is rendered more difficult by the fact that the iron does not melt at the heat developed by the combustion of the charcoal, and therefore it does not separate from those mechanically mixed impurities which are found in the iron ore. In this way it would be impossible to produce large quantities of iron cheaply, because after every operation it would be necessary to clean out the apparatus in which the ore was heated with charcoal. This is obviated by the following very remarkable property of iron: at a high temperature it is capable of combining with a small quantity (from 2 to 5 p.c.) of carbon, and then forms *cast iron*, which easily *melts* in the heat developed by the combustion of charcoal in air. For this reason metallic iron is not obtained directly from the ore, but is only formed after the further treatment of the cast iron; the first product extracted from the ore being cast iron. The fused mass disposes itself in the furnace below the slags—that is, the impurities of the ore fused by the heat of the furnace. If these impurities did not fuse

[5] The reduction of iron oxides by hydrogen belongs to the order of the reversible reactions (Chapter II.), and is therefore determined by a limit which is here expressed by the attainment of the same pressure as in the case where hydrogen acts on iron oxides, and as in the case where (at the same temperature) water is decomposed by metallic iron. The calculations referring to this matter were made by Henri Sainte-Claire Deville (1870). Spongy iron was placed in a tube having a temperature t, one end of which was connected with a vessel containing water at 0° (vapour tension = 4·6 mm.) and the other end with a mercury pump and pressure gauge which determined the limiting tension attained by the dry hydrogen p (subtracting the tension of the water vapour from the tension observed). A tube was then taken containing an excess of iron oxide. It was filled with hydrogen, and the tension p_1 of the hydrogen which remained when the water condensed at 0° was taken.

t =	200°	440°	860°	1040°
p =	95·9	25·8	12·8	9·2 mm.
p_1 =	—	—	12·8	9·4 mm.

The equality of the pressure (tension) of the hydrogen in both cases is evident. The hydrogen here behaves like the vapour of iron or of its oxide.

When Moissan took ferric oxide, Fe_2O_3, he observed that at 350° it passed into magnetic oxide, Fe_3O_4, at 500° into ferrous oxide, FeO, and at 600° into metallic iron. Wright and Luff (1878), whilst investigating the reduction of oxides, found (*a*) that the temperature of reaction depends on the condition of the oxide taken—for instance, precipitated cupric oxide is reduced by hydrogen at 85°, that obtained by oxidising the metal or from its nitrate at 175°; (*b*) when other conditions are the same, the reduction by carbonic oxide commences earlier than that by hydrogen, and the reduction by hydrogen still earlier than that by charcoal; (*c*) the reduction is effected with greater facility when a greater quantity of heat is evolved during the reaction. Ferric oxide obtained by heating ferrous sulphate to a red heat begins to be reduced by carbonic oxide at 202°, by hydrogen at 260°, by charcoal at 430°, whilst for magnetic oxide, Fe_3O_4, the temperatures are 200°, 290°, and 450° respectively.

they would block up the furnace in which the ore was being smelted, and the uninterrupted continuation of the smelting of the cast iron would not be possible;[6] it would be necessary periodically to cool the furnace and heat it up again, which means a wasteful expense of fuel, and therefore in the production of cast iron the object in view is to obtain all the earthy impurities of the ore in the shape of a fused mass or slag. Only in rare cases does the ore itself form a mass which fuses at the temperature employed, and these cases are even objectionable if much iron oxide is carried away in the slag. The impurities of the ores most often consist of certain mixtures—for instance, a mixture of clay and sand, or a mixture of limestone and clay, or quartz, and often of silica, &c. These impurities do not separate of themselves, or do not fuse—for instance, lime and silica only fuse when subjected to the strongest heat. The difficulty of the industry lies in forming an easily-fusible slag, into which the whole of the foreign matter of the ore would pass and flow down to the bottom of the furnace above the heavier cast iron. This is effected by mixing certain *fluxes* with the ore and charcoal. A flux is a substance which, when mixed with the foreign matter of the ore, forms a fusible vitreous mass or slag. The flux used for silica is limestone with clay; for limestone, silica is used, the best procedure having been arrived at by experiment and by long practice in iron smelting.[7]

[6] The primitive methods of iron manufacture were conducted by intermittent processes in hearths resembling smiths' fires. Commencing with the uninterrupted action of the steam boiler, or the process of lime burning, and up to the continuous preparation and condensation of sulphuric acid or the uninterrupted smelting of iron, every industrial production becomes particularly profitable and complete under the conditions of the continuous action, as far as possible, of all agencies concerned in the production. This continuous method of production is the first condition for the profitable production on the large scale of nearly all industrial products.

[7] The composition of slag suitable for iron smelting most often approaches the following: 50 to 60 p.c. SiO_2, 5 to 20 Al_2O_3, and the rest of the mass consisting of MgO, CaO, MnO, FeO, K_2O, Na_2O. Thus the most fusible slag (according to the observations of Bodeman), contains the alloy $Al_2O_3,4CaO,7SiO_2$. On changing the quantity of magnesia and lime, and especially of the alkalis (the fusibility increases) and of silica (the fusibility decreases), the temperature of fusion changes with the relation between the quantity of oxygen to that in the silica. Slags of the composition RO,SiO_2 are easily fusible, have a vitreous appearance, and are very common. Basic slags approach the composition $2RO,SiO_2$. Therefore, knowing the composition and quantity of the foreign matter in the ore it is at once easy to find the quantity and quality of the flux which must be added to form a suitable slag. The smelting of iron is rendered more complex by the fact that the silica, SiO_2, which enters into the slag and fluxes is capable of forming a slag with the iron oxides. In order that the least quantity of iron may pass into the slag, it is necessary for it to be reduced before the temperature is attained at which the slags are formed (about 1000°), which is effected by reducing the iron, not with charcoal itself, but with carbonic oxide. From this it will be understood how the progress of the whole treatment may be judged by the properties of the slags.

Thus the following materials have to be introduced into the furnace where the smelting of the iron ore is carried on: (1) the iron ore, composed of oxide of iron and foreign matter; (2) the flux required to form a fusible slag with the foreign matter; (3) the carbon which is necessary (*a*) for reducing, (*b*) for combining with the iron reduced to form cast iron, (*c*) principally for the purpose of combustion and the heat generated thereby, necessary not only for reducing the iron and transforming it into cast iron, but also for melting the slags as well as the cast iron—the reaction of reduction is only accomplished at a high temperature—and (4) the air necessary for the combustion of the charcoal. The air is introduced after a preparatory heating (and drying, if moist), in order to economise fuel and to obtain the highest temperature. The air is forced in under pressure by means of a special blast arrangement. This permits of an exact regulation of the heat and rate of smelting. All these component parts necessary for the smelting of iron must be contained in a vertical, that is, *shaft furnace*, which at the base must have a receptacle for the accumulation of the slag and cast iron formed, in order to proceed without interruption. The walls of such a furnace ought to be built of fireproof materials if it be designed to serve for the continuous production of cast iron by charging the ore, fuel, and flux into the mouth of the furnace, forcing a blast of air into the lower part, and running out the molten iron and slag from below. The whole operation is conducted in furnaces known as *blast furnaces*. The annexed illustration represents the vertical section of such a furnace. These furnaces are generally of large dimensions—varying from 50 to 90 feet in height. They are often built against some rising ground or other in order to afford easy access to the most elevated parts where the ore, flux, and charcoal or coke are charged.[8]

[8] The section of a blast furnace is represented by two truncated cones joined at their bases, the higher cone being longer than the lower one; the lower cone is terminated by the hearth, O, or almost cylindrical cavity in which the cast iron and slag collects, one side being provided with apertures for drawing off the iron and slag. The air is blown into the blast furnace through special pipes, T, situated over the hearth, as shown in the section. The air previously passes through a series of cast-iron pipes, heated by the combustion of the carbonic oxide obtained from the upper parts of the furnace, where it is formed as in a 'gas-producer.' The blast furnace acts continuously until it is worn out; the iron is tapped off twice a day, and the furnace is allowed to cool a little from time to time so as not to be spoilt by the increasing heat, and to enable it to withstand a longer campaign.

In order to more thoroughly grasp the chemical process which is effected in blast furnaces, it is necessary to follow the course of the matter charged in at the top and the air passing through the furnace. From 50 to 200 parts of carbon are expended on 100 parts of iron. These quantities are charged into the top of the furnace, in layers, as the cast iron is formed in the lower parts and flowing down to the bottom

The *cast iron* formed in blast furnaces is not always of the same quality. When slowly cooled it is soft, has a grey colour, and is not

causes the whole contents of the furnace to subside, thus forming an empty space at the top, which is again filled up with the afore-mentioned mixture. During its downward course this mixture is subjected to increasing heat. This rise of temperature first drives off the moisture of the ore mixture, and then leads to the formation of

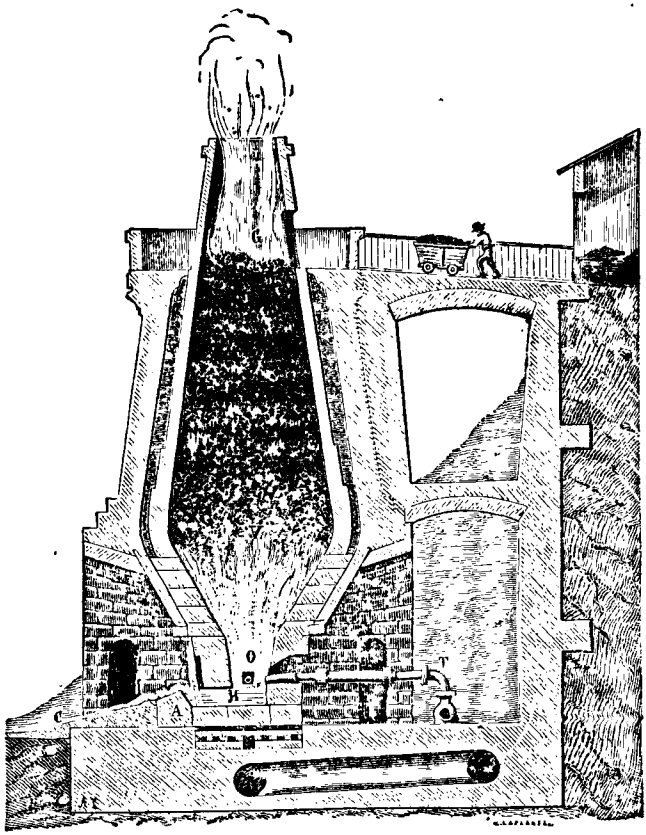


FIG. 93.—Vertical section of a blast furnace.

the products of the dry distillation of coal or charcoal. Little by little the subsiding mass attains a temperature at which the heated carbon reacts with the carbonic anhydride, passing upwards through the furnace, and transforms it into carbonic oxide. This is the reason why carbonic anhydride is not evolved from the furnace, but only carbonic oxide. As regards the ore itself, on being heated to about 600° to 800° it is reduced at the expense of the carbonic oxide ascending the furnace, and formed by the contact of the carbonic anhydride with the incandescent charcoal, so that the reduction process in the blast furnace is without doubt effected *by* the formation and assistance of *carbonic oxide* and not by carbon itself—thus, $Fe_2O_3 + 3CO = Fe_2 + 3CO_2$. The reduced iron on

completely soluble in acids. When treated with acids a residue of graphite remains; it is known as *grey* or soft cast iron. This is the general form of the ordinary cast iron used for casting various objects, because in this state it is not so brittle as in the shape of *white cast iron*, which does not leave particles of graphite when dissolved, but yields its carbon in the form of hydrocarbons. This white cast iron is characterised by its whitish-grey colour, dull lustre, the crystalline structure of its fracture, and such hardness that a file will hardly cut it. When white cast iron is produced (from manganese ore) at high temperatures (and with an excess of lime), and containing but little sulphur and silica, but a considerable amount of carbon (as much as 5 p.c.), it acquires a coarse crystalline structure which increases in

further subsidence and contact with carbon, forms cast iron, which flows to the bottom of the furnace. In these lower layers, where the temperature is most elevated (about 1800°), the foreign matter of the ore finally forms slag, also fusible, with the fluxes. These are the processes accomplished by the mass of the products charged in from above. The air blown in from below, through the so-called *tuyeres*, encounters carbon in the lower layers of the furnace, and burns it, converting it into carbonic anhydride. It is evident that this develops the highest temperature in these lower layers of the furnace, because here the combustion of the carbon is effected at the expense of heated and compressed air. This is very important, because with the assistance of this high temperature the process of forming the slag and that of forming the cast iron are simultaneously terminated in these lower portions of the furnace. The carbonic acid formed in these parts rises higher, encounters incandescent carbon, and forms with it carbonic oxide. This heated carbonic oxide acts as a reducing agent on the iron ore, and is then turned again by it into carbonic anhydride; this gas again meets with carbon, and again forms carbonic oxide, which again acts as a reducing agent. The final transformation of the carbonic anhydride into carbonic oxide is effected in those parts of the furnace where the reduction of the oxides of iron does not take place, but where the temperature is so high as to be sufficient to reduce the carbonic anhydride. The ascending mixture of carbonic oxide and nitrogen of the air is then withdrawn through special lateral apertures formed in the upper cold parts of the furnace walls. The mixture of carbonic oxide and nitrogen is conducted through pipes to those stoves which are used for heating the air, and also sometimes into other furnaces used for the further processes of iron manufacture. The fuel of blast furnaces consists of wood charcoal (this is the best but most expensive material, because it does not contain sulphur), anthracite (for instance, in Pennsylvania, and in Russia at Pastouhoff's works in the Don district), coke, coal, and even wood and peat. It must be borne in mind that the utilisation of naphtha and naphtha refuse would probably give very profitable results in metallurgical processes. Here experiments are absolutely necessary, and particularly important for Russia, because the Caucasus is capable of yielding vast quantities of naphtha. Vapours and gases ought in general to be applied to the metallurgy of iron, which is at present exclusively based on the application of solid fuel.

The process just described is, if it may be so expressed, worked side by side with a series of smaller processes. Thus, for instance, in the blast furnace a considerable quantity of cyanogen compounds are formed. This takes place because the nitrogen of the air blast comes into contact with incandescent carbon and various alkaline matters contained in the foreign matter of the ores. A considerable quantity of potassium cyanide is formed when wood charcoal is employed for iron smelting, as its ash is rich in potash.

proportion to the amount of manganese, and it is then known under the name of 'spiegeleisen' (and 'ferro-manganese').[9]

Cast iron is a material which is either suitable for direct application for casting in moulds or else for working up into *wrought iron* and *steel*. The latter principally differ from cast iron in their containing less carbon—thus, steel contains from 1 p.c. to 0·5 p.c. of carbon and far less silicon and manganese than cast iron; wrought iron does not generally contain more than 0·25 p.c. of carbon and not more than 0·25 p.c. of the other impurities. Thus the essence of the working up of cast iron into steel and wrought iron consists in the removal of the greater part of the carbon. This is effected by means of oxidation, because the oxygen of the atmosphere, oxidising the iron at a high temperature, forms solid oxides with it; and the latter, coming into contact with the carbon contained in the cast iron, are deoxidised, forming wrought iron and carbonic oxide, which is evolved from the mass in a gaseous form. It is evident that the oxidation must be carried on with a molten mass in a state of agitation, so that the oxygen of the air, passing over the surface of the iron, may be brought into contact with the whole mass of carbon contained in the cast iron,

[9] The specific gravity of white cast iron is about 7·5. Grey cast iron has a much lower specific gravity, namely, 7·0. Grey cast iron generally contains less manganese and more silica than white; but both contain from 2 to 3 p.c. of carbon. The difference between the varieties of cast iron depends on the condition of the carbon which enters into the composition of the iron. In white cast iron the carbon is in combination with the iron—in all probability as the compound CFe_4, but perhaps in the state of an indefinite chemical compound resembling a solution. In any case the compound of the iron and carbon in white cast iron is chemically very unstable, because when slightly cooled it decomposes, with separation of graphite, just as a solution when slowly cooled yields a portion of the substance dissolved. However, the separation of carbon in the form of graphite on the transition of white cast iron into grey is never complete; part of the carbon remains in combination with the iron in the same state as it is combined in white cast iron. Indeed, when grey cast iron is treated with acids, the whole of the carbon does not remain in the form of graphite, but a part of it is separated as hydrocarbons, which proves the existence of chemically-combined carbon in grey cast iron. It is sufficient to re-melt grey cast iron and to cool it quickly to transform it into white cast iron. However, it is not carbon alone that influences the properties of cast iron; when it contains a considerable amount of sulphur, cast iron remains white even after having been slowly cooled. The same is observed in cast iron very rich in manganese (5 to 7 p.c.), and in this latter case the fracture is very distinctly crystalline and brilliant. When cast iron contains a large amount of manganese, the quantity of carbon may also be increased. Crystalline varieties of cast iron rich in manganese are in practice called ferro-manganese, and are prepared for the Bessemer process. Grey cast iron not having an uniform structure is much more liable to various changes than dense and thoroughly uniform white cast iron, therefore the latter oxidises much more slowly in air than the former. The cast iron destined for the manufacture of the best kinds of wrought iron and steel ought to contain very little sulphur and phosphorus (not more than 0·05 p.c.). The silicon, manganese, and part of the sulphur oxidise during the processes, and hardly enter into the steel.

or else the operation is effected by means of the addition of oxygen compounds of iron (oxides, ores), as in Martin's process. The molten mass of cast iron is stirred up, and subjected to the oxidising action of the air. Cast iron melts much more easily than wrought iron and steel, and, therefore, as the carbon separates the mass becomes more and more solid; and the degree of hardness forms, to a certain extent, a measure of the amount of carbon separated, and the operation may terminate either in the formation of steel or wrought iron.[10] In any case, the iron used for industrial purposes contains

[10] This direct process of separating the carbon from cast iron is termed *puddling*. It is conducted in reverberatory furnaces (Vol. I. p. 513). The cast iron is placed on the bed of the furnace and melted; through a special aperture the puddler stirs up the oxidising mass of cast iron, compressing the oxides into the molten cast iron. This resembles kneading dough, and the process introduced in England became known as puddling. It is evident that the puddled mass, or bloom, is an heterogeneous substance obtained by mixing, and therefore one part of the mass will still be rich in carbon, another will be poor, some parts will contain oxides not yet reduced, &c. The further treatment of the puddled mass consists in hammering and drawing out into flat pieces, which on being hammered become more homogeneous, and when several pieces are welded together and again hammered out a still more homogeneous mass is obtained. The quality of the steel and iron thus formed depends principally on their uniformity. The want of uniformity depends on the oxides remaining inside the mass, and on the variable distribution of the carbon throughout the mass. In order to obtain a more homogeneous metal for manufacturing articles out of steel, it is drawn into thin rods, which are tied together in bundles and then again hammered out. As an example of what may be reached in this direction, imitation Damascus steel may be cited; it consists of twisted and plaited wire, which is then hammered into a dense mass. (Real damascened wootz steel may be made by melting a mixture of the best iron with graphite ($\frac{1}{100}$) and iron rust; the article is then corroded with acid, and the carbon remains in the form of a pattern.)

Steel and wrought iron are manufactured from cast iron by puddling. They are, however, not only obtained by this method but also by the *bloomery process*, which consists in a fire similar to a blacksmith's forge, fed with charcoal and provided with a blast; a cast-iron pig is little by little pushed into the fire, and portions of it melt and fall to the bottom of the hearth, coming into contact with an air blast, and are thus oxidised. The bloom thus formed is then subjected to further treatment. It is evident that this process is only available when the charcoal used in the fire does not contain any foreign matter which might injure the quality of the iron or steel—for instance, sulphur or phosphorus—and therefore only wood charcoal may be used with impunity, from which it follows that this process can only be carried on where the manufacture of iron can be conducted with this fuel. Coal and coke contain the above-mentioned impurities, and would therefore produce iron of a brittle nature, and thus it would be necessary to have recourse to puddling, where the fuel is burnt on a special hearth, separate from the cast iron, whereby the impurities of the fuel do not come into contact with it. The manufacture of steel from cast-iron may also be conducted in fires; but, in addition to this, it is also now prepared by many other methods. One of the long-known processes is called *cementation*, by which steel is prepared from wrought iron but not from cast iron. For this process strips of iron are heated red-hot for a considerable time whilst immersed in powdered charcoal; during this operation the iron at the surface combines with the charcoal, but the interior contains but little of it; after this the iron strips are re-forged, drawn out again, and cemented anew, repeating the process until a steel of the desired quality is formed—that is, containing the requisite proportion of carbon. The

impurities. *Chemically pure iron* may be obtained by precipitating iron from a solution (a mixture of ferrous sulphate with magnesium sulphate

Bessemer process occupies the front rank among the newer methods (since 1856); it is so called from the name of its inventor. This process consists in running melted cast iron into retorts (converters, holding about 6 tons of cast iron)—that is, egg-shaped receivers, fig. 94, capable of revolving on trunnions (in order to charge in the

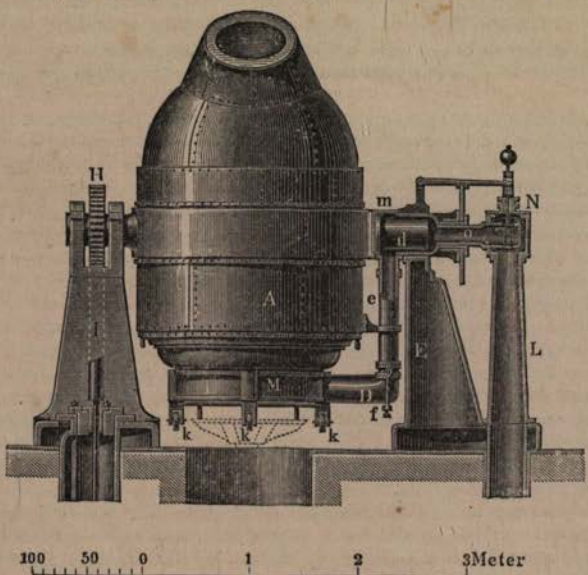


FIG. 94.—Bessemer converter, constructed of iron plate and lined with ganister. The air is carried by the tubes L, O, D to the bottom, M, from which it passes by a number of holes into the converter. The converter is rotated on the trunnion *d* by means of the rack and pinion H, when it is required either to receive molten cast iron from the melting furnaces or to pour out the steel.

cast iron and discharge the steel), and forcing a stream of air through small apertures at a considerable pressure. Combustion of the iron and carbon at an elevated temperature then takes place, resulting from the bubbles of oxygen thus penetrating the mass of the cast iron. The carbon, however, burns to a greater extent than the iron, and therefore a mass is obtained which is much poorer than cast iron in carbon. As the combustion proceeds very rapidly in the mass of metal, the temperature rises to such an extent that even the wrought iron which may be formed remains in a molten condition, whilst the steel, being more fusible than the wrought iron, remains very liquid. In half an hour the mass is ready. The purest possible cast iron is used in the Bessemer process, because sulphur and phosphorus do not burn out like carbon, silicon, and manganese.

The presence of manganese enables the sulphur to be removed with the slags, and the presence of lime or magnesia, which are introduced into the lining of the converter, facilitate the removal of the phosphorus. This basic Bessemer process or *Thomas-Gilchrist process*, introduced about 1880, enables ores containing a considerable amount of phosphorus, which had hitherto only been used for cast iron, to be used for making wrought iron and steel. Naturally, the greatest uniformity will be obtained by re-melting the metal. Steel is re-melted in small wind furnaces, in masses not exceeding 30 kilos; a liquid metal is formed, which may be cast in moulds. A mixture of wrought iron and steel is often used for making cast steel. Large steel castings are made by simul-

or ammonium chloride) by the prolonged action of a feeble galvanic current; the iron may be then obtained as a dense mass. This method,

taneously melting in many furnaces and crucibles; in this way, castings up to 80 tons or more, such as large ordnance, may be made. This molten, and therefore homogeneous, steel is called *cast steel.* Of late years the *Martin's process* for the manufacture of steel has come largely into use; it was invented in France about 1860, and with the use of regenerative furnaces it enables large quantities of cast steel to be made at a time. It is based on the melting of cast iron with iron oxides and iron itself—for instance, pure ores, scrap, &c. There the carbon of the cast iron and the oxygen of the oxide form carbonic oxide, and the carbon therefore burns out, and thus cast steel is obtained from cast iron, providing, naturally, that there is a requisite proportion and corresponding degree of heat. The advantage of this process is that not only do the carbon, silicon, and manganese, but also a great part of the sulphur and phosphorus of the cast iron burn out at the expense of the oxygen of the iron oxides. During the last decade the manufacture of steel and its application for rails, armour plate, guns, boilers, &c., has developed to an enormous extent, thanks to the invention of cheap processes for the manufacture of large masses of homogeneous cast steel, but there is every reason to affirm that the metallurgy of iron is still capable of considerable further improvement. Wrought iron may also be melted, but the heat of a blast furnace is insufficient for this. It easily melts in the oxyhydrogen flame. It may be obtained in a molten state directly from cast iron, if the latter be melted with nitre and sufficiently stirred up. Considerable oxidation then takes place inside the mass of cast iron, and the temperature rises to such an extent that the wrought iron formed remains liquid. A method is also known for obtaining wrought iron directly from rich iron ores by the action of carbonic oxide; the wrought iron is then formed as a spongy mass (which forms an excellent filter for purifying water), and may be worked up into wrought iron or steel either by forging or by dissolving in molten cast iron.

Everybody is more or less familiar with the *difference in the properties of steel and wrought iron.* Iron is remarkable for its softness, pliability, and small elasticity, whilst steel may be characterised by its capability of attaining elasticity and hardness if it be cooled suddenly after having been heated to a definite temperature, or, as it is termed, *tempered.* But if tempered steel be re-heated and slowly cooled, it becomes as soft as wrought iron, and can then be cut with the file and forged, and in general can be made to assume any shape, like wrought iron. In this soft condition it is called *annealed steel.* The transition from tempered to annealed steel takes place, then, in a similar way to the transition from white to grey cast iron. Steel, when homogeneous, has considerable lustre, and has such a fine granular structure that it takes a very high polish. Its fracture clearly shows the granular nature of its structure. The possibility of tempering steel enables it to be used for making all kinds of cutting instruments, which are forged, filed, and cut when the steel is in the annealed condition, and then tempered, ground, polished, &c. The method and temperature of tempering and annealing steel determine its hardness and other qualities. Steel is generally tempered to the required degree of hardness in the following manner. It is first strongly heated (for instance, up to 600°), and then plunged into water—that is, hardened by rapid cooling (it then becomes as brittle as glass). It is then heated until the surface assumes a definite colour, and finally either suddenly or slowly cooled. When steel is heated up to 200°, its surface acquires a yellow colour (surgical instruments); it first of all becomes straw-coloured (razors, &c.), and then gold-coloured; then at a temperature of 250° it becomes brown (scissors), then red, then light blue at 285° (springs), then indigo at 300° (files), and finally sea-green at about 340°. These colours are nothing more than the tints of thin films, like the hues of soap bubbles, and appear on the steel because a thin layer of oxides is formed over its surface. Steel rusts more slowly than wrought iron, and is more soluble in acids than cast iron, but less so than wrought iron. Its specific gravity is about 7·6 to 7·9.

As regards the formation of steel, it was a long time before the process of cementation

proposed by Böttcher and applied by Klein, gives, as R. Lenz showed, iron containing occluded hydrogen, which is disengaged on heating. This

was thoroughly understood, because in this case infusible charcoal permeates unfused wrought iron. Caron showed that this permeation depends on the fact that the charcoal used in the process contains alkalis, which, in the presence of the nitrogen of the air, form metallic cyanides, which, being volatile and fusible, permeate the iron, and, giving up their carbon to the iron, serve as the material for the formation of steel. This explanation is confirmed by the fact that charcoal without alkalis or without nitrogen will not cement iron. Lime with charcoal and in the presence of nitrogen will not cement, because no calcium cyanide is then formed. The charcoal used for cementation acts badly when used over again, as it has lost alkali. The very volatile ammonium cyanide easily conduces to the formation of steel. Although steel is also formed by the action of cyanogen compounds, nevertheless it does not contain more nitrogen than cast or wrought iron (0·01 p.c.), and these latter contain it because their ores contain titanium, which directly combines with nitrogen. Hence the part played by nitrogen in steel is but an insignificant one. It may be useful here to add some information taken from Caron's treatise concerning the influence of foreign matter on the quality of steel. The principal properties of steel are those of tempering and annealing. The compounds of iron with silicon and boron have not these properties. They are more stable than the carbon compound, and this latter is capable of changing its properties; because the carbon in it either enters into combination or else is disengaged, which determines the condition of hardness or softness of steel, as in white and grey cast iron. When slowly cooled, steel splits up into a mixture of soft and carburetted iron; but, nevertheless, the carbon does not separate from the iron. If such steel be again heated, it forms a uniform compound, and hardens when rapidly cooled. If the same steel as before be taken and heated a long time, then, after being slowly cooled, it becomes much more soluble in acid, and leaves a residue of pure carbon. This shows that the combination between the carbon and iron in steel becomes destroyed when subjected to heat, and the steel becomes iron mixed with carbon. Such *burnt* steel cannot be tempered, but may be corrected by continued forging in a heated condition, which has the effect of distributing the carbon equally throughout the whole mass. After the forging, if the iron be pure and the carbon has not burnt out, steel is again formed, which may be tempered. If steel be repeatedly or strongly heated, it becomes burnt through and cannot then be tempered or annealed; the carbon separates from the iron, and this is effected more easily if the steel contains more impurities which are capable of forming stable combinations with iron, such as silicon, sulphur, or phosphorus. If there be much silicon, it occupies the place of the carbon, and then continued forging will not compel the carbon once separated to re-enter into combination. Such steel is easily burnt through and cannot be corrected; but, when burnt through, it is hard, but cannot be annealed—this is tough steel, the lower kind. Iron which contains sulphur and phosphorus cements badly, combines but little with carbon, and steel of this kind is brittle, both hot and cold. Iron in combination with the above-mentioned substances cannot be annealed by slow cooling, showing that these compounds are more stable than that of carbon and iron, and therefore they prevent the formation of the latter. Such metals as tin and zinc combine with iron, but not with carbon, and form a brittle mass which cannot be annealed and is deleterious to steel. Manganese and tungsten, on the contrary, are capable of combining with charcoal; they do not hinder the formation of steel, but even remove the injurious effects of other admixtures (by transforming these admixed substances into new compounds and slags), and are therefore ranked with the substances which act beneficially on steel; but, nevertheless, the best steel which is capable of renewing most often its primitive qualities after burning or hot forging is that which is the purest.

The properties of ordinary *wrought iron* are well known. The best iron is the most tenacious—that is to say, that which does not break up when struck with the hammer

galvanic deposition of iron is used for making galvanoplastic *clichés*, which are distinguished for their great hardness. Electro-deposited iron is brittle, but if heated (after the separation of the hydrogen) it becomes soft. If pure ferric hydroxide, which is easily prepared by the precipitation of solutions of ferric salts by means of ammonia, be taken, and heated in a stream of hydrogen, it forms, first of all, a dull black powder which ignites of its own accord in air (pyrophoric iron), and then a grey powder of pure iron. The powdery substance first obtained is an iron suboxide; when thrown into the air it

or bent, and yet at the same time is sufficiently hard. There is, however, a distinction between hard and soft iron. Generally the softest iron is the most tenacious, and can best be welded, drawn into wire, sheets, &c. Hard, especially tough, iron is often characterised by its breaking when bent, and is therefore very difficult to work, and objects made from it are less serviceable in many respects. Hard, tough iron is most suitable for a few objects—such, for instance, as rails, tyres, &c. Soft iron is most adapted to making wire and sheet iron and such small objects as nails. Soft iron is characterised by its attaining a fibrous fracture after forging, whilst tough iron preserves its granular structure after this operation. Certain sorts of iron, although fairly soft at the ordinary temperature, become brittle when heated and are difficult to weld. These sorts are less suitable for being worked up into small objects. The variety of the properties of iron depends on the impurities which it contains. In general, the iron used in the arts still contains carbon and always a certain quantity of silicon, manganese, sulphur, phosphorus, &c. A variety in the proportion of these component parts changes the quality of the iron. In addition to this the change which soft wrought iron, having a fibrous structure, undergoes when subjected to repeated blows and vibrations is considerable; it then becomes granular and brittle. This to a certain degree explains the want of stability of some iron objects—such as truck axles, which must be renewed after a certain term of service, otherwise they become brittle. It is evident that there are innumerable intermediate transitions from wrought iron to steel and cast iron.

It is worthy of attention to point out that steel, besides temper, possesses many various properties, a review of which may be made in the classification of the *sorts of steel* (1878, Cockerell). (1) *Very mild steel* contains from 0·05 to 0·20 p.c. of carbon, breaks with a weight of 40 to 50 kilos. per square millimetre, and has an extension of 20 to 30 p.c.; it may be welded, like wrought iron, cannot be tempered, is used in sheets for boilers, armour plate and bridges, nails, rivets, &c., as a substitute for wrought iron; (2) *mild steel*, from 0·20 to 0·35 p.c. of carbon, resistance to tension 50 to 60 kilos., extension 15 to 20 p.c., not easily welded, and tempers badly, used for axles, rails, and railway tyres, for cannons and guns, and for parts of machines destined to resist bending and torsion; (3) *hard steel*, carbon 0·35 to 0·50 p.c., breaking weight 60 to 70 kilos. per square millimetre, extension 10 to 15 p.c., cannot be welded, takes a temper; used for rails, all kinds of springs, swords, parts of machinery in motion subjected to friction, spindles of looms, hammers, spades, hoes, &c.; (4) *very hard steel*, carbon 0·5 to 0·65 p.c., tensile breaking weight 70 to 80 kilos., extension 5 to 10 p.c., does not weld, but tempers easily; used for small springs, saws, files, knives, and similar instruments.

The quantity of steel manufactured yearly in Europe is about one million tons, and in North America about half this quantity; in England alone the annual output of cast iron is above 8 million tons, and that of the whole of Europe and America about 15 million tons. Russia contributes but a small part proportionally—namely, about one-fortieth of the whole production—although the Ural, the Don district, and other parts of Russia represent the combination of all advantageous conditions for the future successful development of a vast iron industry. More than three-quarters of the cast iron produced is consumed in the manufacture of wrought iron and steel.

ignites, forming the oxide Fe_3O_4. If the heating in hydrogen be continued, more water and pure iron, which does not ignite spontaneously, will be obtained. If a small quantity of iron be fused in the oxyhydrogen flame (with an excess of oxygen) in a piece of lime and mixed with powdered glass, pure molten iron will be formed, because in the oxyhydrogen flame iron melts and burns, but the substances mixed with the iron oxidise before it. The oxidised impurities here either disappear (carbonic anhydride) in a gaseous form, or (silica, manganese oxide, and others) turn into slag—that is, fuse with the glass. Pure iron has a silvery white colour and a specific gravity of 7·84; it melts at a temperature higher than the melting-points of silver, gold, and steel. But pure iron becomes soft at a temperature considerably below that at which it melts, and may then be easily forged, welded, and rolled or drawn into sheets and wire.[11] Pure iron may be rolled into an exceedingly thin sheet, weighing less than a sheet of ordinary paper of the same size. This ductility is the most important property of iron in all its forms, and is most marked with sheet iron, and least so with cast iron, whose ductility, compared with wrought iron, is small, but is still very considerable when compared with other substances—such, for instance, as rocks.[12]

[11] Gore (1869), Tait, Barret, Tchernoff, Osmond, and others observed that at a temperature approaching 600°—that is, between dark and bright red heat—all kinds of wrought iron undergo a peculiar change called *recalescence*, or a spontaneous rise of temperature. If iron is considerably heated and allowed to cool, it may be observed that at this temperature the cooling stops—that is, the latent heat is disengaged, corresponding with a change in condition. The specific heat, electrical conductivity, magnetic, and other properties then also change. In tempering, the temperature of recalescence must not be reached, and so also in annealing, &c. It is evident that a change of the internal condition is here encountered, exactly similar to the transition from a solid to a liquid, although there is no evident physical change. It is probable that attentive study would lead to the discovery of a similar change in other substances.

It may be remarked here that iron begins to give out light (in the dark) at a temperature of 405°, and the melting-point of iron must be considered to be far lower than that of platinum (1775°), namely about 1400° to 1600°. According to information supplied by A. T. Skinder's experiments at the Oboukoff Steel Works, 140 volumes of liquid molten steel give 128 volumes of solid metal. By means of a galvanic current of great intensity and dense charcoal as one electrode, and iron as the other, Bernadoss welded iron and fused holes through sheet iron. Soft wrought iron, like steel and soft malleable cast iron, may be melted in Siemens' regenerative furnaces, and in furnaces heated with naphtha.

[12] The particles of steel are linked together or connected more closely than those of the other metals; this is shown by the fact that it only breaks with a tensile strain of 80 kilos. per sq. mm., whilst wrought iron only withstands about 60 kilos., cast iron 10, copper 35, silver 23, platinum 30, wood 10, glass 1. The elasticity of iron, steel, and other metals, also, is expressed by the so-called *coefficient of elasticity*. Let a rod be taken whose section $= n$ sq. mm. and length L; if a weight, P, be hung from the extremity of it, it will lengthen to l. The less it lengthens under other equal conditions, the more elastic the material, if it resumes its original length when the weight is removed. It has been

The chemical properties of iron have been already rendered clear by the preceding statements. Iron *rusts* in air at the ordinary temperature—that is to say, it becomes covered with a layer of iron oxides. Here, without doubt, the moisture of the air plays a part, because in dry air iron does not oxidise at all, and also because, more particularly, ammonia is always found in iron rust; the ammonia must arise from the action of the hydrogen of the water, at the moment of its separation, on the nitrogen of the air. Highly-polished steel does not rust nearly so readily, but in moist air, and especially if moistened with water, it easily becomes coated with rust. As rust depends on the access of moisture, iron may be preserved from rust by coating it with substances which prevent the moisture having access to it. Thus arises the practice of covering iron objects with paraffin,[13] varnish, oil, paints, or enamelling it with a glassy-looking flux possessing the same coefficient of expansion as iron, or with a dense scoria (formed by the heat of superheated steam), or with a compact coating of various metals. Wrought iron, both as sheet iron and other objects, cast iron, and steel are often coated with tin, copper, lead, nickel, and similar metals, which prevent contact with the air. These metals preserve iron very effectually from rust if they form a completely compact surface, but in those places where the iron becomes exposed, either accidentally or from wear, rust appears much more quickly than on a uniform iron surface, because, as regards these metals (and also as regards the rust), the iron will then behave as an electro-positive pole in a galvanic couple, and hence will attract oxygen. A coating of zinc does not produce this inconvenience, because iron is electro-negative with reference to zinc, in consequence of which galvanised iron does not easily rust, and even an iron boiler containing

shown by experiment that the increase in length l, due to elasticity, is directly proportional to the length L and the weight P, and inversely proportional to the section n, but changes with the material, and therefore $lKn = PL$, where K is the coefficient of elasticity of the material. Evidently $K = \frac{PL}{ln}$. Therefore, if $n = 1$ and $l = L$ (that is, the length is doubled), then $K = P$, and, therefore, the coefficient of elasticity expresses that weight (in kilos. per sq. mm.) under which a rod having a square section taken as 1 (we take 1 sq. mm.) acquires double the length by tension. Naturally in practice materials do not withstand such a lengthening, under a certain weight or at the limit of elasticity they stretch permanently (undergo deformation), and therefore the limit of elasticity serves as a characteristic of the metal in addition to the coefficient of elasticity k and the tensile breaking weight. The following data concerning the elasticity of various metals are according to Bertheim and others, fractions being neglected, as the elasticity of metals varies not only with the temperature but also with forging, purity, &c. The magnitude of k for steel and iron is 19000, copper and brass 9000 to 11000, silver 7000, glass 6000, lead and wood 1700.

[13] Paraffin is one of the best preservatives for iron against oxidation in the air. I found this by experiments about 1860, and immediately published the fact. This method is now very generally applied.

some lumps of zinc rusts less than one without zinc.[14] Iron oxidises at a high temperature (Chapter III.), forming *iron scale*, Fe_3O_4, composed of ferrous and ferric oxides, and, as has been seen, decomposes water and acids, with the evolution of hydrogen. It is also capable of decomposing salts and oxides of other metals, which property is applied in the arts for the extraction of copper, silver, lead, tin, &c. For this reason, iron is soluble in the solutions of many salts—for instance, in cupric sulphate, with precipitation of copper and formation of ferrous sulphate.[15] When iron *acts on acids* it always *forms ferrous compounds* —that is, those corresponding with the magnesium compounds—and hence two atoms of hydrogen are replaced by one atom of iron. Strongly oxidising acids like nitric acid may transform the ferrous salt which is forming into the higher degree of oxidation or ferric salt (corresponding with the sesquioxide, Fe_2O_3), but this is a secondary phenomenon. Iron, although easily soluble in dilute nitric acid, loses this property when plunged into strong fuming nitric acid; after this operation it even loses the property of solubility in other acids until the external coating formed by the action of the strong nitric acid is mechanically removed. This condition of iron is termed the passive state. *The passive condition* of iron depends on the formation, on its surface, of a coating of oxide due to the iron being acted on by the lower oxides of nitrogen contained in the fuming nitric acid.[16] Strong nitric acid, which does not contain these lower oxides, does not render iron passive, but it is only necessary to add some alcohol or other reducing agent which forms these lower oxides in the nitric acid, and the iron will assume the passive state. Passive iron has a practical application in galvanic couples.

Iron readily combines with non-metals—for instance, with chlorine,

[14] Based on the rapid oxidation of iron and its increase in volume in the presence of water and salts of ammonium, a packing is used for water mains and steam pipes which is tightly hammered into the socket joints. This packing consists of a mixture of iron filings and a small quantity of sal-ammoniac (and sulphur) moistened with water; after a certain lapse of time, especially after the pipes have been used, this mass swells to such an extent that it hermetically seals the joints of the pipes.

[15] Here, however, a ferric salt may also be formed (when all the iron has dissolved and the cupric salt is still in excess), because the cupric salts are reduced by ferrous salts. Cast iron is also dissolved.

[16] Powdery reduced iron is passive with regard to nitric acid of a specific gravity of 1·37, but when heated the acid acts on it. This passiveness disappears in the magnetic field. Saint Edme attributes the passiveness of iron (and nickel) to the formation of nitride of iron on the surface of the metal, because he observed that when heated in dry hydrogen ammonia is evolved by passive iron.

Remsen observed that if a strip of iron be immersed in acid and placed in the magnetic field, it is principally dissolved at its fore part—that is, the acid acts more feebly at the poles.

iodine, bromine, sulphur, and even with phosphorus and carbon; but, on the other hand, the property of combining with metals is but little developed in it—that is to say, it does not easily form alloys. Mercury, which acts on most metals, does not act directly on iron, and the *iron amalgam*, or solution of iron in mercury, which is used for electrical machines, is only obtained in a particular way—namely, with the co-operation of a sodium amalgam, in which the iron dissolves and by means of which it is reduced from solutions of its salts.

When iron acts on acids it forms ferrous salts of the type FeX_2, and in the presence of air and oxidising agents they change by degrees into ferric salts of the type FeX_3. This faculty of passing from the ferrous to the ferric state is still further developed in ferrous hydroxide. If sodium hydroxide be added to a solution of ferrous sulphate, or green vitriol, $FeSO_4$,[17] a white precipitate of ferrous hydroxide, FeH_2O_2, is obtained; but on exposure to the air, even under water, it turns green, becomes grey, and finally turns brown, which is due to the oxidation that it undergoes. Ferrous hydroxide is very sparingly soluble in water; the solution has, however, a clearly alkaline reaction,

[17] *Iron vitriol* or *green vitriol*, sulphate of iron or ferrous sulphate, crystallises from solutions, like magnesium sulphate, with seven molecules of water, $FeSO_4,7H_2O$. This salt is not only formed by the action of iron on sulphuric acid, but also by the action of moisture and air on iron pyrites, especially when previously roasted ($FeS_2+O_2=FeS+SO_2$), and in this condition it easily absorbs the oxygen of damp air ($FeS+O_4=FeSO_4$). A vast amount of green vitriol is obtained in many processes, very often as a bye product. Ferrous sulphate, like all the ferrous salts, has a pale greenish colour hardly perceptible in solution. If it be desired to preserve it without change—that is, so as not to contain ferric compounds—it is necessary to keep it hermetically sealed. This is best done by forcing out the air by means of sulphurous anhydride or ether; sulphurous anhydride, SO_2, removes oxygen from ferric compounds, which might be formed, and is itself changed into sulphuric acid, and therefore the oxidation of the ferrous compound does not take place in its presence. Unless these precautions are taken, green vitriol turns brown, partly changing into the ferric salt—that is, having absorbed oxygen. When turned brown, it is not completely soluble in water, because during its oxidation a certain amount of free insoluble ferric oxide is formed: $6FeSO_4+O_3=2Fe_2(SO_4)_3+Fe_2O_3$. In order to cleanse such mixed green vitriol from the oxide, it is necessary to add some sulphuric acid and iron and boil the mixture; the ferric salt is then transformed into the ferrous state: $Fe_2(SO_4)_3+Fe=3FeSO_4$. The solubility of ferrous sulphate in water is given in Vol. I. p. 71, Note 24.

Green vitriol is used for the manufacture of Nordhausen sulphuric acid, for preparing ferric oxide, in many dye works (for preparing the indigo vats and reducing blue indigo to white), and in many other processes; it is also a very good disinfectant, and is the cheapest salt from which other compounds of iron may be obtained.

The other ferrous salts (excepting the yellow prussiate, which will be mentioned hereafter) are but little used, and it is therefore unnecessary to dwell upon them. We will only mention *ferrous chloride*, which, in the crystalline state, has the composition $FeCl_2,4H_2O$. It is easily prepared; for instance, by the action of hydrochloric acid on iron, and in the anhydrous state by the action of hydrochloric acid gas on metallic iron at a red heat. The anhydrous ferrous chloride then volatilises in the form of colourless, cubic crystals.

which is due to its being a fairly energetic basic oxide. In any case, ferrous oxide is far more energetic than ferric oxide, so that if ammonia be added to a solution containing a mixture of a ferrous and ferric salt, at first ferric hydroxide only will be precipitated. If barium carbonate, $BaCO_3$, be shaken up in the cold with ferrous salts, it does not precipitate them—that is, does not change them into ferrous carbonate; but it completely separates all the iron from the ferric salts in the cold, according to the equation $Fe_2Cl_6 + 3BaCO_3 + 3H_2O = Fe_2O_3,3H_2O + 3BaCl_2 + 3CO_2$. If ferrous hydroxide be boiled with a solution of potash, the water is decomposed, hydrogen is evolved, and the ferrous hydroxide is oxidised. The ferrous salts are in all respects similar to the salts of magnesium and zinc; they are isomorphous with them, but differ from them in that the ferrous hydroxide is not soluble either in aqueous potash or ammonia. In the presence of an excess of ammonium salts, however, a certain proportion of the iron is not precipitated by alkalis and alkali carbonates, which fact points to the formation of double ammonium salts.[18] The ferrous salts have a dull *greenish* colour, and form solutions also of a pale green colour, whilst the ferric salts have a *brown* or reddish-brown colour. The ferrous salts, being capable of oxidation, form very active reducing agents—for instance, under their action gold chloride, $AuCl_3$, deposits metallic gold, nitric acid is transformed into lower oxides, and the highest oxides of manganese also pass into the lower forms of oxidation. All these reactions take place with especial ease in the presence of an excess of acid. This depends on the fact that the ferrous oxide, FeO (or salt), acting as a reducing agent, turns into ferric oxide, Fe_2O_3 (or salt), and in the ferric state it requires more acid for the formation of a normal salt than in the ferrous condition. Thus in the normal ferrous sulphate, $FeSO_4$, there is one equivalent of iron to one equivalent of sulphur (in the sulphuric radicle), but in the ferric salt, $Fe_2(SO_4)_3$, there is one equivalent of iron to one and a half of sulphur in the form of the elements of sulphuric acid.[19]

[18] Ferrous sulphate, like magnesium sulphate, easily forms double salts—for instance, $(NH_4)_2SO_4,FeSO_4,6H_2O$. This salt does not oxidise in air so readily as green vitriol.

[19] The transformation of ferrous oxide into ferric oxide is not completely effected in air, as then only a part of the suboxide is turned into ferric oxide. Here most often the so-called magnetic oxide of iron is produced, containing atomic quantities of the suboxide and oxide—namely, $FeO,Fe_2O_3 = Fe_3O_4$. This substance, as has been already seen, is found in nature and in iron scale. It is also formed when most ferrous and ferric salts are heated in air; thus, for instance, when ferrous carbonate is heated it loses the elements of carbonic anhydride, and magnetic oxide remains. This oxide of iron is attracted by the magnet, and is hence called magnetic oxide, although it does not always show magnetic properties. If magnetic oxide be dissolved in any acid—for instance, hydrochloric—which does not act as an oxidising agent, a ferrous salt is first formed and

The most simple oxidising agent for transforming ferrous into ferric salts is chlorine in the presence of water—for instance, $2FeCl_2 + Cl_2 = Fe_2Cl_6$, or, generally speaking, $2FeO + Cl_2 + H_2O = Fe_2O_3 + 2HCl$. When such a transformation is required it is best to add potassium chlorate and hydrochloric acid to the ferrous solution; chlorine is formed by their mutual reaction, which in this case acts as an oxidising agent. Nitric acid, although more slowly, produces a similar effect. Ferrous salts may be completely and rapidly oxidised into ferric salts by means of some of the higher metallic oxides—for instance, chromic or permanganic acid, $HMnO_4$, in the presence of acids—for example, $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$. This reaction is easily observed by the change of colour, and its termination is easily seen, because potassium permanganate forms solutions of a bright red colour, and when added to a solution of ferrous salts the above reaction immediately takes place *in the presence of acid*, and the solution then fades, because all the substances formed colour the solutions but very feebly. Directly all the ferrous compound has passed into the ferric state, any excess of permanganate which is added communicates a red colour to the liquid.

Thus when ferrous salts are acted on by oxidising agents, they pass into the ferric form, and under the action of reducing agents the reverse reaction occurs. Sulphuretted hydrogen may, for instance, be used for this complete transformation, for under its influence ferric salts are reduced with separation of sulphur—for example, $Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S$. Sodium thiosulphate acts in a similar way: $Fe_2Cl_6 + Na_2S_2O_3 + H_2O = 2FeCl_2 + Na_2SO_4 + 2HCl + S$. Metallic iron and metallic zinc,[20] in the presence of acids, or sodium amalgam, &c.,

ferric oxide remains, which is also capable of passing into solution. The best way of preparing the hydrate of the magnetic oxide is by decomposing a mixture of ferrous and ferric salts with ammomia; it is, however, indispensable to pour this mixture into the ammonia, and not *vice versâ*, as then the ferrous oxide would at first be alone precipitated, and then the ferric oxide. The compound thus formed has a bright green colour, and when dried forms a black powder. Other combinations of ferrous with ferric oxide are known, as are also compounds of ferric oxide with other bases. Thus, for instance, there are known compounds of 4 molecules of ferrous oxide and 1 of ferric oxide, and also 6 of ferrous and 1 of ferric oxide. These are also magnetic, and are formed by heating iron in air. The magnesium compound MgO,Fe_2O_3 is prepared by passing gaseous hydrochloric acid over a heated mixture of magnesia and ferric oxide. Crystalline magnesium oxide is then formed, and black, shiny, octahedral crystals of the above-mentioned composition. This compound is analogous to the aluminates—for instance, to spinel.

[20] Copper and cuprous salts also reduce ferric oxide to ferrous oxide, and are themselves turned into cupric salts. The essence of the reactions is expressed by the following equations: $Fe_2O_3 + Cu_2O = 2FeO + 2CuO$; $Fe_2O_3 + Cu = 2FeO + CuO$. This fact is made use of in analysing copper compounds, the quantity of copper being ascertained by the amount of ferrous salt obtained. An excess of ferric salt is required to complete the reaction. Here we have an example of reverse reaction; the ferrous oxide or its salt in

act like hydrogen, and have also a similar reducing action, and this furnishes the best method for reducing ferric salts into ferrous salts—for instance, $Fe_2Cl_6 + Zn = 2FeCl_2 + ZnCl_2$. Thus *the transition from ferrous salts to ferric salts and vice versâ is always possible.*[21]

Ferric oxide, or *sesquioxide of iron*, Fe_2O_3, is found in nature, and is artificially prepared in the form of a red powder by many methods. Thus after heating green vitriol a red oxide of iron remains, called *colcothar*, which is used as an oil paint, principally for painting wood. The same substance in the form of a very fine powder (rouge) is used for polishing glass, steel, and other objects. If ferrous sulphate is mixed with an excess of common salt and heated, crystalline ferric oxide will be formed, having a dark violet colour, and resembling some natural varieties of this substance. When iron pyrites is heated for preparing sulphurous anhydride, ferric oxide also remains behind. On the addition of alkalis to a solution of ferric salts, a brown precipitate of ferric hydroxide is formed, which when heated (even when boiled in water, that is, at about 100°, according to Tomassi) easily parts with the water, and leaves red anhydrous ferric oxide. Pure ferric oxide does not show any magnetic properties, but when heated to a white heat it loses oxygen and is converted into the magnetic oxide. Anhydrous ferric oxide which has been heated to a high temperature is with difficulty soluble in acids (but is soluble when heated in strong acids, and also when fused with potassium hydrogen sulphate), whilst ferric hydroxide, at all events that which is precipitated from salts by means of alkalis, is very readily soluble in acids. The precipitated *ferric hydroxide* has the composition $2Fe_2O_3,3H_2O$, or $Fe_4H_6O_9$. If this ordinary hydroxide is rendered anhydrous (at 100°), at a certain moment it, as it were, burns—that is, loses a certain quantity of heat.

the presence of alkali transforms the cupric oxide into cuprous oxide and metallic copper, as observed by Lovel, Knopp, and others.

[21] We will mention those reactions by means of which it may be ascertained whether the ferrous compound has been entirely converted into a ferric compound or *vice versâ*. There are two substances which give the best reactions for this purpose: potassium ferricyanide, $FeK_3C_6N_6$, and thiocyanate, KCNS. The first salt gives with ferrous salts a blue precipitate of an insoluble salt, having a composition $Fe_5C_{12}N_{12}$; but with ferric salts it does not form any precipitate, and only gives a brown colour, and therefore when transforming a ferrous salt into a ferric salt, the completion of the transformation may be detected by taking a drop of the liquid on paper or white china and adding a drop of the ferricyanide solution. If a blue precipitate be formed, then part of the ferrous salt still remains; if there is none, it means that the transformation is complete. The thiocyanate does not give any marked coloration with ferrous salts; but with ferric salts in the most diluted state it forms a bright red soluble compound, and therefore when transforming a ferric salt into a ferrous salt, we must proceed as before, testing a drop of the solution with thiocyanate, when the absence of a red colour will prove the total transformation of the ferric salt into the ferrous state, and if a red colour is apparent it shows that the transformation is not yet complete.

This self-incandescence depends on internal displacement produced by the transition of the easily-soluble (in acids) variety into the difficultly-soluble variety, but does not depend on the loss of water, because the anhydrous oxide undergoes the same change. In addition to this there exists a ferric hydroxide, or hydrated oxide of iron, just as difficultly soluble in acids as strongly-heated anhydrous iron oxide is. This hydroxide losing water, or after the loss of water, does not undergo such self-incandescence, because no such state of internal displacement occurs (loss of energy or heat) with it as that which is peculiar to the ordinary oxide of iron. The ferric hydroxide which is difficultly soluble in acids has the composition $Fe_2O_3\,H_2O$. This hydroxide is obtained by a prolonged ebullition of water in which is suspended ferric hydroxide prepared by the oxidation of ferrous oxide, and also sometimes by similar treatment of the ordinary hydroxide after it has been for a long time in contact with water. The transition of one hydroxide to another is apparent by a change of colour; the easily-soluble hydroxide is redder, and the sparingly-soluble hydroxide more yellow in colour.[22]

The normal salts of the composition Fe_2X_6 correspond with ferric oxide; for example, the exceedingly volatile *ferric chloride*, Fe_2Cl_6, which is easily prepared in the anhydrous state by the action of chlorine on heated iron.[23] Such also is the *normal ferric nitrate*, $Fe_2(NO_3)_6$;

[22] The two ferric hydroxides are not only characterised by the above-mentioned properties, but also by the fact that the first hydroxide forms immediately with potassium ferrocyanide, $K_4FeC_6N_6$, a blue colour depending on the formation of prussian blue, whilst the second hydroxide does not give any reaction whatever with this salt. The first hydroxide is entirely soluble in nitric, hydrochloric, and all other acids; whilst the second sometimes (not always) forms a brick-coloured liquid, which appears turbid and does not give the reactions peculiar to the ferric salts (Péan de Saint Gilles, Scheurer-Kestner). In addition to this, when the smallest quantity of an alkaline salt is added to this liquid, ferric oxide is precipitated. Thus a colloidal solution is formed (hydrosol), which is exactly similar to silica hydrosol (Chapter XVII.), according to which example the hydrosol of ferric oxide may be obtained.

If ordinary ferric hydroxide is dissolved in acetic acid, a solution of the colour of red wine is obtained, which has all the reactions characteristic of ferric salts. But if this solution (formed in the cold) is heated to the boiling-point, its colour is very rapidly intensified, a smell of acetic acid becomes apparent, and the solution then contains a new variety of ferric oxide. If the boiling of the solution be continued, acetic acid is evolved, and the modified ferric oxide is precipitated. If the evaporation of the acetic acid be prevented (in a closed vessel), and the liquid be heated for some time, the whole of the ferric hydroxide then passes into the soluble form, and if some alkaline salt be added (to the hydrosol formed), the whole of the ferric oxide is then precipitated in its insoluble form. This method may be applied for separating ferric oxide from solutions of its salts.

All phenomena observed respecting ferric oxide (colloidal properties, various forms, formation of double basic salts) demonstrate that this substance, like silica, alumina, lead hydroxide, &c., is polymerised, that the composition is represented by $(Fe_2O_3)_n$.

[23] The ferric compound which is most used in practice (for instance, in medicine, for

it is obtained by dissolving iron in an excess of nitric acid, taking care as far as possible to prevent any rise of temperature.[24] The normal salt separates from the brown solution when it is concentrated under

cauterising, stopping bleeding, &c.—Oleum Martis) is *ferric chloride*, Fe_2Cl_6, obtained in solution—for instance, as $2Fe_2O_3,3H_2O+14HCl$. It is obtained in the anhydrous state by the action of chlorine on heated iron. The experiment is carried on in a porcelain tube, and a solid *volatile substance* is then formed in the shape of brilliant violet scales which very readily absorb moisture from the air, and when heated with water decompose into crystalline ferric oxide and hydrochloric acid: $Fe_2Cl_6+3H_2O=6HCl+Fe_2O_3$. Ferric chloride is so volatile that the density of its vapours may be determined. At 440° it is equal to 164·0 referred to hydrogen; the formula Fe_2Cl_6 corresponds with a density of 162·5. An aqueous solution of this salt has a brown colour. On evaporating and cooling this solution, crystals separate containing 6 or 12 molecules of H_2O. Ferric chloride is not only soluble in water, but also in alcohol (similarly to magnesium chloride, &c.) and in ether. If the latter solutions are exposed to the rays of the sun they become colourless, and deposit ferrous chloride, $FeCl_2$, chlorine being disengaged. After a certain lapse of time, the aqueous solutions of ferric chloride decompose with precipitation of a basic salt, thus demonstrating the instability of ferric chloride, like the other salts of ferric oxide. This salt is much more stable in the form of double salts, as are all the ferric salts and also the salts of many other feeble bases. Potassium or ammonium chloride forms with it very beautiful red crystals of a double salt, having the composition $Fe_2Cl_6,4KCl,2H_2O$. When a solution of this salt is evaporated, it decomposes, with separation of potassium chloride.

[24] The normal ferric salts are decomposed by heat and even by water, forming basic salts, which may be prepared in various ways. Generally ferric hydroxide is dissolved in solutions of ferric nitrate; if it contains a double quantity of iron the basic salt is then formed, which, therefore, contains Fe_2O_3 (in the form of hydroxide) $+2Fe_2(NO_3)_6=3Fe_2O(NO_3)_4$, a salt of the type Fe_2OX_4. Probably water enters into its composition. With considerable quantities of ferric oxide, insoluble basic salts are obtained containing various amounts of ferric hydroxide. Thus when a solution of the above-mentioned basic salt is boiled, a precipitate is formed containing $4(Fe_2O_3)_8,2(N_2O_5),3H_2O$, which probably contains $2Fe_2O_2(NO_3)_2+2Fe_2O_3,3H_2O$. If a solution of basic nitrate be sealed in a tube and then immersed in boiling water, the colour of the solution changes just in the same way as if a solution of ferric acetate had been employed. The solution obtained smells strongly of nitric acid, and on adding a drop of sulphuric or hydrochloric acid the insoluble variety of hydrated ferric oxide is precipitated.

Normal ferric *orthophosphate* is soluble in sulphuric, hydrochloric and similar acids, but insoluble in others, such as, for instance, acetic acid. The composition of this salt in the anhydrous state is $FePO_4$, because in orthophosphoric acid there are three atoms of hydrogen, and iron, in the ferric state, replaces the three parts of hydrogen. This salt is obtained from ferric acetate, which, with disodium phosphate, forms a *white precipitate* of $FePO_4$, containing water (on boiling, 2 mol. H_2O). It is simplest to proceed as follows: A solution of ferric chloride (yellowish red colour) is mixed with a solution of sodium acetate in excess (this must be done first and not afterwards). The liquid then assumes an intense brown colour which demonstrates the formation of a certain quantity of ferric acetate; then the disodium phosphate directly forms a white gelatinous precipitate of ferric phosphate. Here the whole of the iron may be precipitated, and the liquid from brown then becomes colourless. If this normal salt be immersed in orthophosphoric acid, the crystalline acid salt $FeH_3(PO_4)_2$ is formed. If there is an excess of ferric oxide in the solution, the precipitate will consist of the basic salt. If ferric phosphate be dissolved in hydrochloric acid, and ammonia be added, on heating, a salt is precipitated which, after continued washing in water and heating (to remove the water), has the composition $Fe_4P_2O_{11}$—that is, $2Fe_2O_3,P_2O_5$. In an aqueous condition this salt may be considered as ferric hydroxide, $Fe_2(OH)_6$, in which $(OH)_3$ is replaced by the equivalent (judging from

a bell jar over sulphuric acid. This salt, $Fe_2(NO_3)_6,9H_2O$, then crystallises in well-formed and completely colourless crystals,[25] which deliquesce in air, melt at 35°, and are soluble in and decomposed by water. The decomposition may be seen from the fact that the solution is brown and does not yield the whole of the salt again, but gives partly basic salt. The normal salt is completely decomposed with great facility by heating with water, even at 130°, and this is made use of for removing iron (and also certain other oxides of the form R_2O_3) from many other bases (of the form RO) whose nitrates are far more stable.

Iron forms one more oxide besides the ferric and ferrous oxides; this contains twice as much oxygen as the former, but is so very unstable that it can neither be obtained in the free state nor as a hydrate. Whenever such conditions of double decomposition occur as should allow of its separation in the free state, it decomposes into oxygen and ferric oxide. It is known in the state of salts, and is only stable in the presence of alkalis, and forms salts with them which have a decidedly alkaline reaction; it is therefore a feebly acid oxide. Thus when small pieces of iron are heated with nitre or potassium chlorate, a potassium salt of the composition K_2FeO_4 is formed, and therefore the hydrate corresponding with this salt should have the composition H_2FeO_4. It is called *ferric acid*. Its anhydride ought to contain FeO_3 or Fe_2O_6—twice as much oxygen as ferric oxide. If a solution of potassium ferrate is mixed with acid, the free hydrate ought to be formed, but it immediately decomposes

$$(2K_2FeO_4 + 5H_2SO_4 = 2K_2SO_4 + Fe_2(SO_4)_3 + 5H_2O + O_3)$$

the formation of Na_3PO_4 from 3NaHO) group PO_4. Whenever ammonia is added to a solution containing an excess of ferric salt and a certain amount of phosphoric acid, a precipitate is formed containing the whole of the phosphoric acid in the mass of the ferric oxide.

Ferric oxide is characterised as a feeble base, and also by the fact of its forming double salts—for instance, *potassium iron alum*, which has a composition $Fe_2(SO_4)_3,K_2SO_4,24H_2O$ or $FeK(SO_4)_2,12H_2O$. It is obtained in the form of almost colourless or light rose-coloured large octahedra of the regular system by simply mixing solutions of potassium sulphate and the ferric sulphate obtained by dissolving ferric oxide in sulphuric acid.

[25] It would seem that all normal ferric salts are colourless, and that the brown colour which is peculiar to the solutions is really due to basic ferric salts. A remarkable example of the seeming change of colour of salts is represented by the ferrous and ferric oxalates. The former in a dry state has a yellow colour, although, as a rule, the ferrous salts are green, and the latter is colourless or pale green. When the normal ferric salt is dissolved in water it is, like many salts, probably decomposed by the water into acid and basic salt, and the latter communicates a brown colour to the solution. Iron alum is almost colourless, is easily decomposed by water, and is the best proof of our supposition. The study of the phenomena peculiar to ferric nitrate might, in my opinion, give a very useful addition to our knowledge of the aqueous solutions of salts. Ferrous

oxygen being evolved. If a small quantity of acid be taken, or if a solution of potassium ferrate be heated with solutions of other metallic salts, ferric oxide is separated, for instance :

$$2CuSO_4 + 2K_2FeO_4 = 2K_2SO_4 + O_3 + Fe_2O_3 + 2CuO.$$

Both these oxides are naturally deposited in the form of hydrates. This shows that not only the hydrate H_2FeO_4, but also the salts of the heavy metals corresponding with this higher oxide of iron, are not formed by reactions of double decomposition. The solution of potassium ferrate naturally acts as a powerful oxidising agent ; for instance, it transforms manganous oxide into the dioxide, sulphurous into sulphuric acid, oxalic acid into carbonic anhydride and water, &c.[26]

Iron thus combines with oxygen in three proportions : RO, R_2O_3, and RO_3. It might have been expected that there would be intermediate stages RO_2 and R_2O_5, but for iron these are unknown. The lower oxide has a distinctly basic character, the higher is feebly acid. The only one which is stable in the free state is ferric oxide, Fe_2O_3 ; the suboxide, FeO, absorbs oxygen, and ferric anhydride, FeO_3, evolves it. It is also the same for other elements ; the character of each is determined by the relative degree of stability of the known oxides. The salts FeX_2 correspond with the suboxide, the salts FeX_3 or Fe_2X_6 with the sesquioxide, and FeX_6 represents those of ferric acid, as its potassium salt is $FeO_2(OK)_2$, corresponding with K_2SO_4, K_2MnO_4, K_2CrO_4, &c. Iron therefore forms compounds of the types FeX_2, FeX_3, and FeX_6, but this latter, like the type NX_5, does not appear separately, but only when X represents heterogeneous elements or groups ; for instance, for nitrogen in the form of $NO_2(OH)$, NH_4Cl, &c., for iron in the form of $FeO_2(OK)_2$. But still the type FeX_6 exists, and therefore FeX_2 and FeX_3 are compounds like ammonia, NH_3, which are capable of further combinations up to FeX_6 and further, which is expressed in the

oxalate, and its double salt with potassium oxalate, act as powerful reducing agents, and the latter is on this account used in photography (as a developer).

[26] If chlorine be passed through a strong solution of potassium hydroxide in which hydrated ferric oxide is suspended, the turbid liquid acquires a dark pomegranate red colour and contains potassium ferrate : $10KHO + Fe_2O_3 + 3Cl_2 = 2K_2FeO_4 + 6KCl + 5H_2O$. The chlorine must not be in excess, otherwise the salt is again decomposed, although the mode of decomposition is unknown; however, ferric chloride and potassium chlorate are probably formed. Another way in which the above-described salt is formed is also remarkable; a galvanic current (from 6 Grove elements) is passed through cast-iron and platinum electrodes into a strong solution of potassium hydroxide. The cast-iron electrode is connected with the positive pole, and the platinum electrode is surrounded by a porous earthen cylinder. Oxygen ought to be evolved at the cast-iron electrode, but it is used up in oxidation, and a dark solution of potassium ferrate is then formed about it. It is remarkable that the cast iron cannot be replaced by wrought iron.

property of ferrous and ferric salts of forming compounds with water of crystallisation, double and basic salts, whose stability is determined by the quality of the elements included in the types FeX_2 and FeX_3. When the molecule Fe_2Cl_6 is produced instead of $FeCl_3$, this complication of the type also occurs. Therefore complex compounds may be expected to correspond with ferrous and ferric oxides. Amongst these the series of cyanogen compounds is particularly interesting; their formation and character is not only determined by the property which iron possesses of forming complex types, but also by the similar faculty of the cyanogen compounds, which, like nitriles (Chapter IX.), have clearly developed properties of polymerisation and in general of forming complex compounds.

In the cyanogen compounds of iron, two degrees might be expected: $Fe(CN)_2$, corresponding with ferrous oxide, and $Fe(CN)_3$, corresponding with ferric oxide. There are actually, however, many other known compounds, intermediate and far more complex. They correspond with the double salts so easily formed by metallic cyanides. The two following double salts are particularly well known, very stable, often used, and easily prepared. *Potassium ferrocyanide*, or *yellow prussiate of potash*, a double salt of cyanide of potassium and ferrous cyanide, has the composition $FeC_2N_2,4KCN$, its crystals contain 3 mol. of water: $K_4FeC_6N_6,3H_2O$. The other is *potassium ferricyanide* or *red prussiate of potash* or *Gmelin's salt*, containing cyanide of potassium with ferric cyanide; its composition is $Fe(CN)_3,3KCN$ or $K_3FeC_6N_6$. Its crystals do not contain water. The second differs from the first in its containing, not four but, only three atoms of potassium, and is obtained from the first by the action of chlorine, which removes one atom of the potassium. A whole series of other ferrocyanic compounds correspond with these ordinary salts.

Before treating of the preparation and properties of these two remarkable and very stable salts, it must be observed that with ordinary reagents neither of them gives the same double decompositions as the other ferrous and ferric salts, nor exhibits the characteristic properties of the potassium cyanide which they contain. Thus these salts have a neutral reaction, are unchanged by air, dilute acids, or water, unlike potassium cyanide and even some of its double salts. When solutions of these salts are treated with potassium hydroxide, they do not give a precipitate of ferrous or ferric hydroxides, neither are they precipitated by sodium carbonate. This led the earlier investigators to recognise special independent groupings in them. The yellow prussiate was considered to contain the complex radicle FeC_6N_6 combined with potassium, namely with K_4, and K_3 was attributed to the red

prussiate, or else another radicle $Fe_2C_{12}N_{12}$ combined with K_6 was assumed to be present. This was confirmed by the fact that whilst in both salts any other metal, even hydrogen, might be substituted for potassium, the iron remained unexchangeable, just as nitrogen in the cyanogen, ammonium, and nitrates does not enter into double decomposition, being in the state of the complex radicles CN, NH_4, NO_2. Such a representation is, however, completely superfluous for the explanation of the peculiarities in the reactions of such compounds as double salts. If a magnesium salt which can be precipitated by potassium hydroxide does not form a precipitate in the presence of ammonium chloride, it is very clear that it is owing to the formation of a soluble double salt which is not decomposed by alkalis. And there is no necessity to account for the peculiarity of reaction of a double salt by the formation of a new complex radicle. In the same way also, in the presence of an excess of tartaric acid cupric salts do not form a precipitate with potassium hydroxide, because a double salt is formed. These peculiarities are more easily understood in the case of cyanogen compounds than in all others, because all cyanogen compounds, as unsaturated compounds, show a marked tendency to complexity. This tendency is satisfied in double salts. The appearance of a peculiar character in double cyanides is the more easily understood as in the case of potassium cyanide itself, and also in hydrocyanic acid, a great many peculiarities have been observed which are not encountered in those haloid compounds, potassium chloride and hydrochloric acid, with which it was usual to compare cyanogen compounds. These peculiarities become more comprehensible on comparing cyanogen compounds with ammonium compounds. Thus in the presence of ammonia the reactions of many compounds change considerably. If, in addition to this, it is remembered that the presence of many carbon (organic) compounds frequently completely disturbs the reaction of salts, the peculiarities of many double cyanides will appear still less strange, because they contain carbon. The fact that the presence of carbon or another element in the compound produces a change in the reactions, may be likened to the action of oxygen, which, when entering into a combination, also very materially changes the nature of reactions. Chlorine is not detected by silver nitrate if it is in the form of potassium chlorate, $KClO_3$, as it is detected in potassium chloride, KCl. The iron in ferrous and ferric compounds varies in its reactions. In addition to the above-mentioned facts, consideration ought to be given to the circumstance that the mutability of nitric acid disappears or undergoes considerable modification in its alkali salts, and in general the properties of a salt often differ much from those of the acid. Every

double salt ought to be regarded as a peculiar kind of saline compound; potassium cyanide is, as it were, a basic, and ferrous cyanide an acid, element. They may be unstable in the separate state, but form a stable double compound when combined together; the act of combination disengages the energy of the elements, and they, so to speak, saturate each other. Naturally, all this is not a definite explanation, but then the admission of a special complex radicle can even less be regarded as such.

Potassium ferrocyanide, $K_4FeC_6N_6$, is very easily formed by mixing solutions of ferrous sulphate and potassium cyanide. First, a white precipitate of ferrous cyanide, FeC_2N_2, is formed, which becomes blue on exposure to air, but is soluble in an excess of potassium cyanide, forming the ferrocyanide. The same yellow prussiate is obtained on heating animal nitrogenous charcoal or animal matters—for instance, horn, leather cuttings, &c.—with potassium carbonate in iron vessels,[27] the mass formed being afterwards boiled with water with exposure to air, potassium cyanide first appearing, which gives yellow prussiate. In this manner it is manufactured on the large scale, and is called 'yellow prussiate' ('prussiate de potasse,' Blutlaugensalz). The animal charcoal may be exchanged for wood charcoal, permeated with potassium carbonate and heated in air—that is, nitrogen; the mass thus produced is then boiled in water with ferric oxide.[28]

It is easy to substitute other metals for the potassium in the yellow prussiate. The hydrogen salt or hydroferrocyanic acid, $H_4FeC_6N_6$, is obtained by mixing strong solutions of yellow prussiate and hydrochloric acid. If ether be added and the air be excluded, the acid is obtained directly, in the form of a white, scarcely crystalline precipitate which becomes blue on exposure to air (like ferrous cyanide from the formation of blue compounds of ferrous and ferric cyanides, and it is on this account used in cotton printing). It is soluble in water and alcohol, but not in ether, has marked acid properties, decomposes car-

[27] The sulphur of the animal refuse here forms the compound $FeKS_2$, which, by the action of potassium cyanide, yields potassium sulphide, thiocyanate, and ferrocyanide.

[28] Potassium ferrocyanide may also be obtained from prussian blue by boiling with a solution of potassium and hydroxide, and from the ferricyanide by the action of alkalis and reducing substances (because the red prussiate is a product of oxidation produced by the action of chlorine: a ferric salt is reduced to a ferrous salt), &c. On evaporation the solution yields large pliable crystals containing 3 molecules of water, which is easily expelled by heating above 100°. 100 parts of water at the ordinary temperature are capable of dissolving 25 parts of this salt; its sp. gr. is 1·83. When ignited it forms potassium cyanide and iron carbide, FeC_2. Oxidising substances change it into potassium ferricyanide. With strong sulphuric acid it gives carbonic oxide, and with dilute sulphuric acid, when heated, prussic acid is evolved according to the equation: $2K_4FeC_6N_6 + 3H_2SO_4 = K_2Fe_2C_6N_6 + 3K_2SO_4 + 6HCN$; hence in the yellow prussiate K_2 replaces Fe.

bonates, which renders it possible to readily prepare ferrocyanides of the metals of the alkalis and alkaline earths; these are readily soluble, have a neutral reaction, and resemble the yellow prussiate. Solutions of these salts form precipitates with the salts of other metals, because the ferrocyanides of the heavy metals are insoluble. Here the whole of the potassium of the yellow prussiate, or only a part of it, is exchanged for an equivalent quantity of the heavy metal. Thus, when a cupric salt is added to a solution of yellow prussiate, a red precipitate is obtained which still contains half the potassium of the yellow prussiate:

$$K_4FeC_6N_6 + CuSO_4 = K_2CuFeC_6N_6 + K_2SO_4.$$

But if the process be reversed (the salt of copper will then be in excess) the whole of the potassium will be exchanged for copper, forming a reddish-brown precipitate, $Cu_2FeC_6N_6,9H_2O$. This reaction, and also those similar to it, are very sensitive, and may be used for testing metals in solution, more especially as the colour of the precipitate very often shows a marked difference when one metal is exchanged for another. Zinc, cadmium, lead, antimony, tin, silver, cuprous and aurous salts form *white* precipitates; cupric, uranium, titanium, and molybdenum salts form *reddish-brown*; those of nickel, cobalt, and chromium, *green* precipitates; *with ferrous salts*, ferrocyanide forms, as has been already mentioned, a *white* precipitate—namely, $Fe_2FeC_6N_6$, or FeC_2N_2—which turns blue on exposure to air, and, with ferric salts, a *blue precipitate* called *prussian blue*. Here the potassium is replaced by iron, the reaction being expressed thus: $2Fe_2Cl_6 + 3K_4FeC_6N_6 = 12KCl + Fe_4Fe_3C_{18}N_{18}$, the latter formula expressing the composition of prussian blue. It is therefore the compound $4Fe(CN)_3 + 3Fe(CN)_2$. The yellow prussiate is prepared in chemical works on a large scale, especially for the manufacture of this blue pigment, which is used for dyeing cloth and other fabrics, and also as one of the ordinary blue paints. It is insoluble in water, and the stuffs are therefore dyed by first soaking them in a solution of a ferric salt, and then in a solution of yellow prussiate. However, if there be an excess of yellow prussiate, complete substitution between potassium and iron does not occur, and *soluble blue* is formed: $KFe_2(CN)_6 = KCN,Fe(CN)_2,Fe(CN)_3$. This blue salt is colloidal, is soluble in pure water, but insoluble and precipitated when other salts—for instance, potassium or sodium chloride—are present, even in small quantities, and is therefore first obtained as a precipitate.[29]

[29] Skraup obtained this salt both from potassium ferrocyanide with ferric chloride and from ferricyanide with ferrous chloride, which evidently shows that it contains iron

Potassium ferricyanide, or *red prussiate* of potash, $K_3FeC_6N_6$, is called 'Gmelin's salt,' because this savant obtained it by the action of chlorine on a solution of the yellow prussiate: $K_4FeC_6N_6 + Cl = K_3FeC_6N_6 + KCl$. The reaction is due to the ferrous salt being changed by the action of the chlorine into a ferric salt. It separates from solutions in anhydrous, finely-formed prisms of a red colour, but the solution has an olive colour; in 100 parts of water, at 10°, 37 parts of the salt are dissolved, and at 100° 78 parts.[30] The red prussiate gives a blue precipitate with ferrous salts, called *Turnbull's blue*, very much like prussian blue (and the soluble blue), because it also contains ferrous cyanide and ferric cyanide, although in another propor-

in both the ferric and ferrous states. With ferrous chloride it forms prussian blue, and with ferric chloride Turnbull's blue.

Prussian blue was discovered in the beginning of the past century by a Berlin manufacturer, Diesbach. It was then prepared, as it sometimes is also at present, directly from potassium cyanide obtained by heating animal charcoal with potassium carbonate. The mass thus obtained is dissolved in water, and alum is added to the solution in order to saturate the free alkali, and then a solution of green vitriol is added which has previously been sufficiently exposed to the air to contain both ferric and ferrous salts. If the solution of potassium cyanide is mixed with a solution containing both salts, prussian blue will be formed, because it is a compound of ferrous cyanide, FeC_2N_2, and ferric cyanide, $Fe_2C_6N_6$. A ferric salt with potassium ferrocyanide forms a blue colour, because ferrous cyanide is obtained from the first salt and ferric cyanide from the second. During the preparation of this compound alkali must be avoided, as otherwise the precipitate would contain oxides of iron. Prussian blue has not a crystalline structure; it forms a blue mass with a copper-red metallic lustre. Both acids and alkalis act on it. The action is at first confined to the ferric salt it contains. Thus alkalis form ferric oxide and ferrocyanide in solution: $2Fe_2C_6N_6,3FeC_2N_2 + 12KHO = 2(Fe_2O_3,3H_2O) + 3K_4FeC_6N_6$. Various ferrocyanides may be thus prepared. Prussian blue is soluble in an aqueous solution of oxalic acid, forming blue ink. In air, when exposed to the action of light, it fades; but in the dark again absorbs oxygen and becomes blue, which fact is also sometimes noticed in blue cloth. An excess of potassium ferrocyanide renders prussian blue soluble in water, although insoluble in various saline solutions—that is, it converts it into soluble blue. Strong hydrochloric acid likewise dissolves prussian blue.

[30] Much chlorine must not be taken in preparing this compound, otherwise the reaction goes further. It is easy to find when the action of the chlorine on potassium ferrocyanide must cease; it is only necessary to take a sample of the liquid and add a solution of a ferric salt to it. If there is a precipitate of prussian blue formed, then more chlorine must be added, as there is still some undecomposed ferrocyanide, because the ferricyanide does not give a precipitate with ferric salts. Potassium ferricyanide, as well as the ferrocyanide, easily exchanges its potassium for hydrogen and various metals by double decomposition. With the salts of tin, silver, and mercury it forms yellow precipitates, and with those of uranium, nickel, cobalt, copper, and bismuth brown precipitates. The lead salt under the action of sulphuretted hydrogen forms lead sulphide and a hydrogen salt or acid, $H_3FeC_6N_6$, corresponding with potassium ferricyanide, which is soluble, crystallises in red needles, and resembles hydroferrocyanic acid, $H_4FeC_6N_6$. Under the action of reducing agents—for instance, sulphuretted hydrogen, copper—potassium ferricyanide is changed into ferrocyanide, especially in the presence of alkalis, and thus forms a rather energetic *oxidising agent*—capable, for instance, of changing manganous oxide into dioxide.

tion, being thus formed : $3FeCl_2+2K_3FeC_6N_6=6KCl+Fe_3Fe_2C_{12}N_{12}$, or $3FeC_2N_2,Fe_2C_6N_6$; whilst in Prussian blue we have Fe_7Cy_{18}, and here Fe_5Cy_{12}. A ferric salt ought to form ferric cyanide, $Fe_2C_6N_6$, with red prussiate, but ferric cyanide is soluble, and therefore there is no precipitate, and the liquid only becomes brown.[31]

If chlorine and sodium are representatives of independent groups of elements, the same may also be said of iron. Its nearest analogues alone show, besides a similarity in character, a likeness as regards physical properties and a proximity in atomic weight. Iron occupies a medium position amongst its nearest analogues, both with respect to properties and faculty of forming saline oxides, and also as regards atomic weight. On the one hand, cobalt, 58, and nickel, 59, approach iron, 56 ; they are metals of a more basic character, they do not form

[31] It is important to mention a series of readily crystallisable salts formed by the action of nitric acid on potassium and other ferrocyanides and ferricyanides. These salts contain the elements of nitric oxide, and are therefore called *nitro-(nitroso) ferricyanides (nitroprussides)*. Most often a crystalline sodium salt is obtained, $Na_2FeC_5N_6O,2H_2O$. In its composition this salt differs from the red sodium salt, $Na_3FeC_6N_6$, by the fact that in it one molecule of sodium cyanide, NaCN, is replaced by nitric oxide, NO. In order to prepare it, potassium ferrocyanide in powder must be mixed with five-sevenths of its weight of nitric acid mixed with an equal volume of water. The mixture is at first left at the ordinary temperature, and then heated in a water-bath. Here ferricyanide is first of all formed (as shown by the liquid giving a precipitate with ferrous chloride), which then disappears (no precipitate with ferrous chloride), and forms a green precipitate. The liquid, when cooled, deposits crystals of nitre. The liquid is then strained off and mixed with sodium carbonate, boiled, filtered, and evaporated ; sodium nitrate and the salt described are deposited in crystals. It separates in prisms of a red colour. Alkalis and salts of the alkaline earths do not give precipitates : they are soluble, but the salts of iron, zinc, copper, and silver form precipitates where sodium is exchanged with these metals. It is remarkable that the sulphides of the alkali metals give with this salt an intense bright purple coloration. This series of compounds was discovered by Gmelin and studied by Playfair and others (1849).

This series to a certain extent resembles the nitro-sulphide series described by Roussin. Here the primary compound consists of black crystals, which are thus obtained :—Solutions of potassium hydrosulphide and nitrite are mixed, and the mixture is agitated whilst ferric chloride is added, then boiled and filtered ; on cooling, *black crystals* are deposited, having the composition $Fe_6S_5(NO)_{10},H_2O$ (Rosenberg), or, according to Demel, $FeNO_2,NH_2S$. They have a slightly metallic lustre, and are soluble in water, alcohol, and ether. They absorb the latter as easily as calcium chloride absorbs water. In the presence of alkalis these crystals remain unchanged, but with acids they evolve nitric oxides. It is affirmed that there are several compounds which are capable of interchanging, and correspond with Roussin's salt. Here we enter into the series of the nitrogen compounds which have been as yet but little investigated, and will most probably in time form most instructive material for studying the nature of that element. These series of compounds are as unlike the usual saline compounds of inorganic chemistry as are organic hydrocarbons. There is no necessity to describe these series in detail, because their connection with other compounds is not yet clear, and they have not yet any application ; but, all the same, their investigation gives promise of opening out other realms of knowledge in the future of chemistry.

stable acids or higher degrees of oxidation, and are a transition to copper, 63, and zinc, 65. On the other hand, manganese, 55, and chromium, 52, are the nearest to iron ; they form both basic and acid oxides, and are a transition to the metals possessing acid properties. In addition to having atomic weights approximately alike, chromium, manganese, iron, cobalt, nickel, and copper have also nearly the same specific gravity, so that the atomic volumes and the molecules of their analogous compounds are also near to one another (see table at the beginning of this volume). Besides this, the likeness between the above-mentioned elements is also seen from the following :

They form suboxides, RO, fairly energetic bases, isomorphous with magnesia—for instance, the salt $RSO_4,7H_2O$, akin to $MgSO_4,7H_2O$, and $FeSO_4,7H_2O$, or to sulphates containing less water ; with alkali sulphates all form double salts crystallising with $6H_2O$; all are capable of forming ammonium salts, &c.

The lower hydroxides, in the cases of nickel and cobalt, are fairly stable, are not easily oxidised (the nickel compound with more difficulty than cobalt, a transition to copper) ; with manganese, and especially with chromium, they are more easily oxidised than with iron and pass into higher oxides.

They also form oxides of the form R_2O_3, and with nickel, cobalt, and manganese this oxide is very unstable, and is more easily reduced than ferric oxide ; but, in the case of chromium, it is very stable, and forms the ordinary kind of salts. It is isomorphous with ferric oxide, forms alums, is a feeble base, &c. Chromium and manganese are more easily oxidised with alkali and oxygen than iron is, forming salts like potassium ferrate ; but cobalt and nickel are difficult to oxidise, their acids are not known with any certainty, and are, in all probability, still less stable.

If compounds R_2Cl_6 are formed, they are volatile like Fe_2Cl_6. The cyanogen compounds, especially for manganese and cobalt, are very near akin to the corresponding ferrocyanides.

The oxides of nickel and cobalt are more easily reduced to metal than those of iron, but those of manganese and chromium are not reduced so easily as iron, and the metals themselves are not easily obtained in a pure state ; they are capable of forming varieties resembling cast iron.

The metals have a grey iron colour and are very difficult to melt, but nickel and cobalt can be melted in the reverberatory furnace and are more fusible than iron, whilst chromium is more difficult to melt than platinum (Deville).

When incandescent these metals decompose water, but with greater

difficulty as the atomic weight rises, forming a transition to copper, which does not decompose water.

All the compounds of these metals have various colours, which are sometimes very bright, especially in the higher stages of oxidation.

These metals of the iron group are often met with together in nature. Manganese nearly everywhere accompanies iron, and iron is always an ingredient in the ores of manganese. Chromium is found principally as chrome ironstone—that is, a peculiar kind of magnetic oxide where Fe_2O_3 is replaced by Cr_2O_3.

Nickel and cobalt are the same inseparable companions as iron and manganese. The similarity between them even extends to such remote properties as magnetic qualities. In this series of metals we find those which are the most magnetic: iron, cobalt, and nickel. There is even a magnetic oxide among the chromium compounds, such as is unknown in the other series. Nickel easily becomes passive in strong nitric acid. It absorbs hydrogen in just the same way as iron.

In nature *cobalt* is principally found in combination with arsenic and sulphur. *Cobalt arsenide*, or *cobalt speiss*, $CoAs_2$, is found in brilliant crystals of the regular system, principally in Saxony. *Cobalt glance*, $CoAs_2CoS_2$, resembles it very much, and also belongs to the regular system; it is found in Sweden, Norway, and the Caucasus. *Kupfernickel* is a *nickel ore* in combination with arsenic, but of a different composition from cobalt arsenide, having the formula NiAs; it is found in Bohemia and Saxony. It has a copper red colour and is rarely crystalline; it is so called because the miners of Saxony first mistook it for an ore of copper (*kupfer*), but were unable to extract copper from it. *Nickel glance*, $NiS_2,NiAs_2$, corresponding with cobalt glance, is also known. Nickel accompanies the ores of cobalt and cobalt those of nickel, so that they are common companions. The ores of cobalt are worked in the Caucasus in the Government of Elizavetopolsk. Nickel ores formed by aqueous hydrated nickel silicate are found in the Ural (Revdansk). Large quantities of a similar ore are exported into Europe from New Caledonia. Both contain about 12 per cent. of Ni. Cobalt is principally worked up into cobalt compounds, but nickel is generally reduced to the metallic state, which is now often used for alloys—for instance, for coinage in many European States, and for plating other metals, because it does not oxidise. Cobalt arsenide and cobalt glance are principally used for the preparation of cobalt compounds; they are first sorted by discarding the rocky matter, and then roasted. During this process most of the sulphur and arsenic disappear; the arsenious anhydride volatilises with the

sulphurous anhydride and the metal also oxidises.[32] Having nickel oxide and cobalt oxide it is easy to obtain the metals themselves. In order to do this solutions of their salts are treated with sodium carbonate and the carbonates precipitated are heated; the suboxides are thus obtained, and these latter are reduced in a stream of hydrogen, or even by heating with ammonium chloride. They easily oxidise when in the state of powder. When the chlorides of nickel and cobalt are heated in a stream of hydrogen, the metal is deposited in brilliant scales. *Nickel is always much more easily and quickly reduced than cobalt.* Nickel melts more easily than cobalt, and this even furnishes a means of testing the heating powers of a reverberatory furnace. Cobalt fuses at a temperature only a little

[32] The residue from the roasting of cobalt ores is called *zaffre*, and is often met with in commerce. From this the purer compounds of cobalt may be prepared. The ores of nickel are also first roasted, and the oxide dissolved in acid, nickelous salts being then obtained.

The further treatment of cobalt and nickel ores is facilitated if the arsenic can be almost entirely removed, which may be effected by roasting the ore a second time with a small addition of nitre and sodium carbonate; the nitre combines with the arsenic, forming an arsenious salt, which may be extracted with water. The remaining mass is dissolved in hydrochloric acid, mixed with a small quantity of nitric acid. Copper, iron, manganese, nickel, cobalt, &c., pass into solution. By passing hydrogen sulphide through the solution, copper, bismuth, lead, and arsenic are deposited as metallic sulphides; but iron, cobalt, nickel, and manganese remain in solution. If an alkaline solution of bleaching powder be then added to the remaining solution, the whole of the manganese will first be deposited in the form of dioxide, then the cobalt as hydrated cobaltic oxide, and finally the nickel also. It is, however, impossible to rely on this effecting a complete subdivision, because the higher oxides of the three above-mentioned metals have all a black colour; but, after a few trials, it will be easy to find how much bleaching powder is required to precipitate the manganese, and the amount which will precipitate all the cobalt. The manganese may also be removed by precipitation from a mixture of the solutions of both metals (in the form of the 'ous' salts) with ammonium sulphide, and then treating the precipitate with acetic acid or dilute hydrochloric acid, in which manganese sulphide is easily soluble and cobalt sulphide almost insoluble. Further particulars relating to the separation of cobalt from nickel may be found in treatises on analytical chemistry. In practice it is usual to rely on the rough method of separation founded on the fact that nickel is more easily reduced and more difficult to oxidise than cobalt.

In industry, rather impure cobalt compounds are often used, which are converted into *smalt*. This is glass containing a certain amount of cobalt oxide; the glass acquires a bright blue colour from this addition, so that when powdered it may be used as a blue pigment; it is also unaltered at high temperatures, so that it used to take the place now occupied by prussian blue, ultramarine, &c. At present smalt is almost exclusively used for colouring glass and china. To prepare smalt, ordinary impure cobalt ore is taken—*i.e.* zaffre—which is put into a crucible with quartz and potassium carbonate. A fused mass of cobalt glass is thus formed, containing silica, cobalt oxide, and potassium oxide, and a metallic mass remains at the bottom of the crucible, containing almost all the other metals, arsenic, nickel, copper, silver, &c. This metallic mass is called *speiss*, and is used as nickel ore for the extraction of nickel. Smalt usually contains 70 p.c. of silica, 20 p.c. of potash and soda, and about 5 to 6 p.c. of cobaltous oxide; the remainder consisting of other metallic oxides.

lower than does iron. In general, cobalt is nearer to iron than nickel, nickel being nearer to copper. Both nickel and cobalt have magnetic properties like iron, but more feeble. The specific gravity of nickel reduced by hydrogen is 9·1 and that of cobalt 8·9. Fused cobalt has a specific gravity of 8·5, the density of ordinary nickel being almost the same. Nickel has a greyish, silvery white colour; it is brilliant and very ductile, so that the finest wire may be easily drawn from it. This wire has a resistance to tension equal to iron wire. The beautiful colour of nickel, and the high polish which it is capable of receiving and retaining, as it does not oxidise, render it a useful metal for many purposes. It is now very common to cover other metals with a layer of nickel (nickel plating). This is done by a process of electro-plating, using a solution of a nickel salt. The colour of cobalt is darker and redder; it is also ductile, and has a greater tensile resistance than iron. Dilute acids act very slowly on nickel and cobalt; hydrochloric and sulphuric acids, even when diluted, dissolve these metals, but nitric acid may be considered as the best solvent for them. The solutions in every case contain salts corresponding with the ferrous salts—that is, of the composition RX_2.

The most ordinary compounds of cobalt and nickel are the *salts*, CoX_2, NiX_2, *corresponding with the suboxides* of these metals. These salts are similar to the magnesium salts. The salts of nickel in an aqueous condition have a green colour, and form bright green solutions, but in the anhydrous state they most frequently have a yellow colour. The salts of cobalt are generally rose-coloured, and sometimes blue when in the anhydrous state. Their aqueous solutions are rose-coloured. Cobaltous chloride is easily soluble in alcohol, and forms a solution of an intense blue colour.[33]

[33] This change of colour in cobalt chloride has been already alluded to (Vol. I. p. 94). The change of colour, according to some, is dependent on the combination with water, and according to others on polymeric transformation. It enables a solution of cobalt chloride to be used as sympathetic ink. If something be written with cobalt chloride on white paper, it will be invisible on account of the feeble colour of the solution, and when dry nothing can be distinguished. If, however, the paper be heated before the fire, the rose-coloured salt will be changed into the anhydrous blue salt, and the writing will become quite visible, but fade away again when cool.

Nickel sulphate crystallises from neutral solutions at a temperature of from 15° to 20° in *rhombic* crystals containing $7H_2O$. Its form approaches very closely to that of the salts of zinc and magnesium. The planes of a vertical prism for magnesium salts are inclined at an angle of 90° 30′, for zinc salts at an angle of 91° 7′, and for nickel salts at an angle of 91° 10′. Such is also the form of the zinc and magnesium selenates and chromates. Cobalt sulphate containing 7 molecules of water is deposited in crystals of the *monoclinic* system, like the corresponding salts of iron and manganese. The angle of a vertical prism for the iron salt = 82° 20′, for cobalt = 82° 22′, and the inclination of the horizontal pinacoid to the vertical prism for the iron salt = 99° 2′, and for the cobalt

If a solution of potassium hydroxide is added to a solution of a cobalt salt, a blue precipitate of the basic salt will be formed. If a solution of a cobalt salt is heated almost to the boiling-point, and the boiling solution be mixed with a boiling solution of an alkali hydroxide, a *pink precipitate of cobaltous hydroxide*, CoH_2O_2, will be formed. If the presence of air be not completely excluded during the precipitation by boiling, the precipitate will also contain brown cobaltic hydroxide formed by the further oxidation of the cobaltous oxide. Under similar circumstances nickel salts form *a green precipitate of nickelous hydroxide*, the formation of which is not hindered by the presence of ammonium salts, but in that case only requires more alkali to completely separate the nickel. The nickelous oxide obtained by heating the hydroxide, or from the carbonate or nitrate, is a grey powder, easily soluble in acids and easily reduced, but the same substance may be obtained in the crystalline form as an ordinary product from the ores ; it crystallises in regular octahedra, with a metallic lustre, and is of a grey colour. In this state the nickelous oxide almost resists the action of acids.

It is remarkable to note *the relation* of the cobaltous and nickelous hydroxides to *ammonia* ; aqueous ammonia dissolves the precipitate of nickelous hydroxide. The blue ammoniacal solution of nickel resembles the same solution of cupric oxide, but has a somewhat reddish

salt 99° 36′. All the isomorphous mixtures of the salts of magnesium, iron, cobalt, nickel, and manganese have the same form if they contain 7 mol. H_2O ; and if iron or cobalt predominate, if there is an abundance of magnesium, zinc, or nickel, then the crystals have a rhombic form like magnesium sulphate. Therefore, these sulphates are *dimorphous*, but for some the one form is more stable and for others the other. Brooke, Moss, Mitscherlich, Rammelsberg, and Marignac have explained these relations. Brooke and Mitscherlich also supposed that $NiSO_4,7H_2O$ is not only capable of assuming these forms, but also that of the *tetragonal* system, because it is deposited in this form from acid, and especially from slightly-heated solutions (80° to 40°). But Marignac demonstrated that the tetragonal crystals do not contain 7, but 6, molecules of water, $NiSO_4,6H_2O$. He also observed that a solution evaporated at 50° to 70° deposits monoclinic crystals, but of a different form from ferrous sulphate, $FeSO_4,7H_2O$—namely, the angle of the prism is 71° 52′, that of the pinacoid 95° 6′. This salt appeared to be the same with 6 molecules of water as the tetragonal. Marignac also obtained magnesium and zinc salts with 6 molecules of water by evaporating their solutions at a more elevated temperature, and these salts were found to be isomorphous with the monoclinic nickel salt. In addition to this it must be observed that the rhombic crystals of nickel sulphate with $7H_2O$ become turbid under the influence of heat and light, lose water, and change into the tetragonal salt. The monoclinic crystals in time also become turbid, and change their structure, so that the tetragonal form of this salt is the most stable. Let us also add that nickel sulphate in all its shapes forms very beautiful emerald green crystals, which, when heated to 230°, assume a dirty greenish-yellow hue and then contain one molecule of water.

Krüss and Schmidt (1889) recognise in the usual purified salts of nickel and cobalt the presence of a particular as yet uninvestigated substance (perhaps alumina, or some nitrogen compound of cobalt or nickel) which is soluble in fused caustic alkali.

tint. It is characterised by the fact that it dissolves silk in the same way as the ammoniacal cupric oxide dissolves cellulose. Ammonia likewise dissolves the precipitate of cobaltous hydroxide, forming a brownish liquid, which becomes darker in air and finally assumes a bright red hue, absorbing oxygen. The admixture of ammonium chloride prevents the precipitation of cobalt salts by ammonia, and then, if ammonia be added, a brown solution is obtained from which, as in the case of the preceding solution, potassium hydroxide does not separate the cobaltous oxide. Peculiar compounds are produced in this solution; they are comparatively stable, containing ammonia and an excess of oxygen; they bear the name cobaltoamine and cobaltiamine salts. They have been principally investigated by Genth, Frémy, and Jörgenson. Genth found that when a cobalt salt, mixed with an excess of ammonium chloride, was treated with ammonia and exposed to the air, after a certain lapse of time, on adding hydrochloric acid and boiling, a red powder is precipitated and the remaining solution contains an orange salt. The study of these compounds led to the discovery of a whole series of similar salts, some of which correspond with particular higher degrees of oxidation of cobalt.[34] Nickel does not possess this

[34] The cobalt salts may be divided into at least the following six classes:—

(*a*) *Ammonium cobalt salts*, which are simply direct compounds of the cobaltous salts CoX_2 with ammonia, similar to various other compounds of the salts of silver, copper, and even calcium and magnesium, with ammonia. They are easily crystallised from an ammoniacal solution, and have a pink colour. Thus, for instance, when cobaltous chloride in solution is mixed with sufficient ammonia to redissolve the precipitate first formed, octahedral crystals are deposited which have a composition, $CoCl_2,H_2O,6NH_3$. These salts are nothing else but combinations with the ammonia of crystallisation—if it may be thus termed, likening them in this way to combinations with the water of crystallisation. This similarity is evident both from their composition and from their capability of giving off ammonia at various temperatures. The most important point to observe is that all these salts contain 6 molecules of ammonia to 1 atom of cobalt, and this ammonia is held in fairly stable connection. Water decomposes these salts.

(*b*) The solutions of the above-mentioned salts are rendered turbid by the action of the air; they absorb oxygen and become covered with a crust of *oxycobaltamine salts*. The latter are sparingly soluble in aqueous ammonia, have a brown colour, and are characterised by the fact that with warm water *they evolve oxygen*, forming salts of the following category. The nitrate may be taken as an example of this kind of salt; its composition is $CoN_2O_7,5NH_3,H_2O$. It differs from cobaltous nitrate, $Co(NO_3)_2$, in containing an extra atom of oxygen—that is, it corresponds with cobalt dioxide, CoO_2, in the same way that the first salts correspond with cobaltous oxide; they contain 5, and not 6, molecules of ammonia, as if NH_3 had been replaced by O.

(*c*) *The luteocobaltic salts* are thus called because they have a yellow (luteus) colour. They are obtained from the salts of the first kind by submitting them in dilute solution to the action of the air; in this case salts of the second kind are not formed, because they are decomposed by an excess of water, with the evolution of oxygen and the formation of luteocobaltic salts. By the action of ammonia the salts of the fifth kind (roseocobaltic) are also converted into luteocobaltic salts. These last-named salts generally crystallise readily, and have a yellow colour; they are comparatively much more

property of absorbing the oxygen of the air when in an ammonical solution. In order to understand the relation of nickel it is important to observe that cobalt more easily forms a higher degree of oxidation—namely, *sesquioxide of cobalt, cobaltic oxide*, Co_2O_3—than nickel, in the

stable than the preceding ones, and even for a certain time resist the action of boiling water. Boiling aqueous potash liberates ammonia and precipitates hydrated cobaltic oxide, $Co_2O_3,3H_2O$, from them. This shows that the luteocobaltic salts correspond in the same measure with cobaltic oxide, Co_2O_3, as the salts of the first kind correspond with cobaltous oxide, and those of the second kind with the dioxide. When a solution of luteocobaltic sulphate, $Co_2(SO_4)_3,12NH_3,4H_2O$, is treated with baryta, barium sulphate is precipitated, and the solution contains luteocobaltic hydroxide, which is soluble in water, is powerfully alkaline, absorbs the oxygen of the air, and when heated is decomposed, with the evolution of ammonia. This compound therefore corresponds to a solution of cobaltic hydroxide in ammonia. The luteocobaltic salts contain 2 atoms of cobalt and 12 molecules of ammonia—that is, $6NH_3$ to each atom of cobalt, like the salts of the first kind. The CoX_2 salts have a metallic taste, whilst those of luteocobalt and others have a purely saline taste, like the salts of the alkali metals.

(*d*) *The fuscocobaltic salts.* An ammoniacal solution of cobalt salts acquires a brown colour in the air, due to the formation of these salts. They are also produced by the decomposition of salts of the second kind; they crystallise badly, and are separated from their solutions by addition of alcohol or an excess of ammonia. When boiled they give up the ammonia and cobaltic oxide which they contain. Hydrochloric and nitric acids give a yellow precipitate with these salts, which turns red when boiled, forming salts of the next category. The following is an example of the composition of two of the fuscocobaltic salts, $Co_2O(SO_4)_2,8NH_3,4H_2O$ and $Co_2OCl_4,8NH_3,3H_2O$. It is evident that the fuscocobaltic salts are ammoniacal compounds of basic cobaltic salts. The normal cobaltic sulphate ought to have the composition $Co_2(SO_4)_3 = Co_2O_3,3SO_3$; the simplest basic salts will be $Co_2O(SO_4)_2 = Co_2O_3,2SO_3$, and $Co_2O_2(SO_4) = Co_2O_3,SO_3$. The fuscocobaltic salts correspond with the first type of basic salts. They are changed (in concentrated solutions) into oxycobaltamine salts by absorption of one atom of oxygen, $Co_2O_2(SO_4)_2$. The whole process of oxidation will be as follows: first of all Co_2X_4, a cobaltous salt, is in the solution (X a univalent haloid, 2 molecules of the salt being taken), then Co_2OX_4, the basic cobaltic salt (4th series), then $Co_2O_2X_4$, the salt of the dioxide (2nd series). The series of basic salts with an acid, 2HX, forms water and a normal salt, Co_2X_6 (in 3, 5, 6 series). These salts are combined with various amounts of water and ammonia. Under many conditions the salts of fuscocobalt are easily transformed into salts of the next series. The salts of the series that has just been described contain 4 molecules of ammonia to 1 atom of cobalt.

(*e*) *The roseocobaltic salts*, like the luteocobaltic, correspond with the normal cobaltic salts, but contain less ammonia. Thus the sulphate is obtained from cobaltous sulphate dissolved in ammonia and left exposed to the air until transformed into a brown solution of the fuscocobaltic salt; when this is treated with sulphuric acid a crystalline powder of the roseocobaltic salt, $Co_2(SO_4)_3,10NH_3,5H_2O$, separates. The formation of this salt is easily understood: cobaltous sulphate in the presence of ammonia absorbs oxygen, and the solution of the fuscocobaltic salt will therefore contain, like cobaltous sulphate, one part of sulphuric acid to every part of cobalt, so that the whole process of formation may be expressed by the equation: $10NH_3 + 2CoSO_4 + H_2SO_4 + 4H_2O + O$. This salt forms tetragonal crystals of a red colour, slightly soluble in cold, but readily soluble in warm water. When the sulphate is treated with baryta roseocobaltic hydroxide is formed in the solution, which absorbs the carbonic anhydride of the air. It is obtained from the next series by the action of alkalis.

(*f*) The *purpureocobaltic salts* are also products of the direct oxidation of ammoniacal solutions of cobalt salts. They are easily obtained by heating the roseocobaltic salts

presence of hypochlorous acid. If a solution of a cobalt salt be mixed with barium carbonate and an excess of hypochlorous acid be added, or chlorine gas be passed through it, then at the ordinary temperature on shaking, the whole of the cobalt will be separated in the form of

with strong acids. They are to all effects the same as the roseocobaltic salts, only anhydrous. Thus, for instance, the purpureocobaltic chloride, $Co_2Cl_6,10NH_3$, is obtained by boiling the oxycobaltamine salts with ammonia. There is the same distinction between these salts and the preceding ones as between the various compounds of cobaltous chloride with water.

The cobaltamine compounds differ but little essentially from the ammoniacal compounds of other metals. The only difference is that here the cobaltic oxide is obtained from the cobaltous oxide in the presence of ammonia. In any case it is a simpler question than that of the double cyanides. Those forces in virtue of which such a considerable number of ammonia molecules are united with a molecule of a cobalt compound, appertain naturally to the series of those slightly-investigated residual affinities which exist even in the highest degrees of combination of the majority of elements. They are the same forces which lead to the formation of compounds containing water of crystallisation, double salts, and perhaps also isomorphous mixtures. The simplest conception, according to my opinion, of cobalt compounds (much more so than by assuming special complex radicles, like Schiff, Weltzen, Claus, Henning, and others), may be formed by comparing them with other ammoniacal products. Ammonia, like water, combines in various proportions with a multitude of substances. Silver chloride and calcium chloride, just like cobalt chloride, absorb ammonia, forming compounds which are sometimes slightly stable, and easily dissociated, sometimes more stable, in exactly the same way as water combines with certain substances, forming fairly stable compounds called hydroxides or hydrates, or less stable compounds which are called compounds with water of crystallisation. Naturally, the faculty of forming one or the other compound with ammonia, as in the case of water, depends on the property of those elements which enter into the composition of the given substance, and on those kinds of affinity towards which chemists have not as yet turned their attention. If boron fluoride, silicon fluoride, &c., combine with hydrofluoric acid, if platinic chloride, and even cadmium chloride, combine with hydrochloric acid, then these compounds may be regarded as double salts, because acids are salts of hydrogen. But evidently water and ammonia have the same saline faculty, more especially as they, like haloid acids, contain hydrogen, and are both capable of further combination—for instance, ammonia with hydrochloric acid. Therefore it is simpler to compare complex ammoniacal compounds with double salts, hydrates, and similar compounds, as will be seen in the description of the compounds of platinum.

The ammonio-metallic salts present a most developed qualitative and quantitative resemblance to *the hydrated salts of metals*. The composition of the latter is $MX_n mH_2O$, where M = metal, X = the haloid, simple or complex, and m and n the quantity of the haloid and so-called water of crystallisation combined with the salt. The composition of the ammoniacal salts of metals is $MX_n mNH_3$. The water of crystallisation is held by the salt with more or less stability, and some salts even do not retain it at all; some part with water easily when exposed to the air, others when heated, and then with difficulty. In the case of some metals all the salts combine with water, whilst with others only a few, and the water so combined may then be easily disengaged. All this refers equally well to the ammoniacal salts, and therefore the combination of ammonia may be termed *the ammonia of crystallisation*. A colourless, anhydrous cupric salt—for instance, cupric sulphate—when combined with water forms blue and green salts, and violet when combined with ammonia. If steam be passed through anhydrous copper sulphate the salt absorbs water and becomes heated; if ammonia be substituted for the water the heating becomes much more intense, and the salt breaks up into a fine violet powder. With water $CuSO_4,5H_2O$ is formed, and with ammonia $CuSO_4,5NH_3$, the

black cobaltic oxide: $2CoSO_4 + ClHO + 2H_2O = Co_2O_3 + 2H_2SO_4 + HCl$. Under these circumstances nickelous oxide does not immediately form black sesquioxide, but after a considerable space of time it also sepa-

number of water and ammonia molecules retained by the salt being the same in each case, and as a proof of this, and that it is not an isolated coincidence, the remarkable fact must be borne in mind that water and ammonia consecutively, molecule for molecule, are capable of supplanting each other, and forming the compounds $CuSO_4,5H_2O$, $CuSO_4,4H_2O,NH_3$; $CuSO_4,3H_2O,2NH_3$; $CuSO_4,2H_2O,3NH_3$; $CuSO_4,H_2O,4NH_3$, and $CuSO_4,5NH_3$. The last of these compounds was obtained by Henry Rose, and my experiments have shown that more ammonia than this cannot be retained. By adding to a strong solution of cupric sulphate sufficient ammonia to dissolve the whole of the oxide precipitated, and then adding alcohol, Berzelius obtained the compound $CuSO_4,H_2O,4NH_3$, &c. The law of substitution also assists in rendering these phenomena clearer, because a compound of ammonia with water forms ammonium hydroxide, NH_4HO, and therefore these molecules combining with one another may also interchange, as being of equal value. In general, those salts form stable ammoniacal compounds which are capable of forming stable compounds with water of crystallisation; and as ammonia is capable of combining with acids, and as some of the salts formed by slightly energetic bases in their properties more closely resemble acids (that is, salts of hydrogen) than those salts containing more energetic bases, we might therefore expect to find more stable and more easily-formed ammonio-metallic salts with metals and their oxides having weaker basic properties than with those which form energetic bases. This explains why the salts of potassium, barium, &c., do not form ammonio-metallic salts, whilst the salts of silver, copper, zinc, &c., do form them. This consideration also accounts for the great stability of the ammoniacal compounds of cupric oxide compared with silver oxide, because the former is displaced by the latter. It also enables us to see clearly the distinction which exists in the stability of the cobaltamine salts containing salts corresponding with cobaltous oxide, and those corresponding with higher oxides of cobalt, because the latter are weaker bases than cobaltous oxides. *The nature of the forces and quality of the phenomena occurring during the formation of the most stable substances, and of such compounds as crystallisable compounds, are one and the same, although exhibited in a different degree.* This may be confirmed by examining the compounds of carbon, because for this element the nature of the forces acting during the formation of its compounds is well known. Let us take as an example two unstable compounds of carbon. Acetic acid, $C_2H_4O_2$ (specific gravity 1·06), with water forms the hydrate, $C_2H_4O_2,H_2O$, denser (1·07) than either of the components, but unstable and easily decomposed, generally directly referred to as a solution. Such also is the crystalline compound of oxalic acid, $C_2H_2O_4$, with water, $C_2H_2O_4,2H_2O$. Their formation might be predicted as issuing from the hydrocarbon C_2H_6, in which, as in any other, the hydrogen may be exchanged for chlorine, the water residue (hydroxyl), &c. The first substitution product with hydroxyl, $C_2H_5(HO)$, is stable; it can be distilled without alteration, resists a temperature higher than 100°, and then does not give off water. This is ordinary alcohol. The second, $C_2H_4(HO)_2$, can also be distilled without change, but can be decomposed into water and C_2H_4O (ethylene oxide or aldehyde); it boils at about 197°, whilst the first hydrate boils at 78°, a difference of about 100°. The compound $C_2H_3(HO)_3$ will be the third product of such substitution; it ought to boil at about 300°, but does not resist this temperature—it decomposes into H_2O and $C_2H_4O_3$, where only one hydroxyl group remains, and the other part of oxygen is left in the same condition as ethylene oxide, C_2H_2O. There is a proof of this. Glycol, $C_2H_4(HO)_2$, boils at 197°, and forms water and ethylene oxide, which boils at 13° (aldehyde, its isomeride, boils at 21°); therefore the product disengaged by the splitting up of the hydrate boils at 184° lower than the hydrate $C_2H_4(HO)_2$. Thus in exactly the same way the hydrate $C_2H_3(HO)_3$, which ought to boil at about 300°, splits up into water and the product $C_2H_4O_2$, which boils at 117°—that is, nearly 183° lower

rates in the form of sesquioxide, but always later than cobalt. This is due to the relative difficulty of further oxidation of the nickelous oxide. It is, however, possible to oxidise it; if, for instance, the

than the hydrate, $C_2H_3(HO)_5$. But this hydrate splits up before distillation. The above-mentioned hydrate of acetic acid is a similar decomposable hydrate—that is to say, what is called a solution. Still less stability may be expected from the following hydrates. $C_2H_2(HO)_4$ also splits up into water and a hydrate (it contains two hydroxyl groups) called glycollic acid, $C_2H_2O(HO)_2 = C_2H_4O_3$. The next product of substitution will be $C_2H(HO)_5$; it splits up into water, H_2O, and glyoxylic acid, $C_2H_4O_4$ (three hydroxyl groups). The last hydrate which ought to be obtained from C_2H_6, and ought to contain $C_2(HO)_6$, is a crystalline compound of oxalic acid, $C_2H_2O_4$ (two hydroxyl groups), and water, $2H_2O$, which has been mentioned already. The hydrate, $C_2(HO)_6 = C_2H_2O_4,2H_2O$, ought, according to the foregoing reasoning, to boil at about 600° (because the hydrate, $C_2H_4(HO)_2$, boils at about 200°, and the substitution of 4 hydroxyl groups for 4 atoms of hydrogen will raise the boiling-point 400°). It does not resist this temperature, but at a much lower point splits up into water, $2H_2O$, and the hydrate $C_2O_2(HO)_2$, which is also capable of yielding water. Without going into further considerations on this subject, it may be observed that the formation of hydrates or compounds with water of crystallisation of acetic and oxalic acids has thus received an accurate explanation, which was the point we desired to prove in affirming that compounds with water of crystallisation are held together by the same forces as those which act in the formation of other complex substances, and the easy displaceability of the water of crystallisation is only a peculiarity of a completely local character, and not the chief and radical point of distinction. All the above-mentioned hydrates, C_2X_6, or products of their destruction, are actually obtained by the oxidation of the first hydrate, $C_2H_5(HO)$, or common alcohol, by nitric acid (Sokoloff and others).

In conclusion, it may be observed that the elements of the eighth group—that is, the analogues of iron and platinum—according to my opinion, will yield most fruitful results when studied as to combinations with whole molecules, as already shown by the examples of complex ammoniacal, cyanogen, nitro-, and other compounds, which are easily formed in this eighth group, and are remarkable for their stability. This faculty of the elements of the eighth group for forming the complex compounds alluded to, is in all probability connected with the position which the eighth group occupies with regard to the others. Following the seventh, which forms the type RX_7, it might be expected to contain the most complex type, RX_8. This is met with in OsO_4. The other elements of the eighth group, however, only form the lower types RX_2, RX_3, RX_4 . . . . and these accordingly should be expected to complicate themselves into the higher types.

The following reaction may be added to those of the cobaltous and nickelous salts; potassium cyanide forms a precipitate with cobalt salts which is soluble in an excess of the reagent and forms a green solution. On heating this and adding a certain quantity of acid, a double *cobalt cyanide* is formed which corresponds with potassium ferricyanide. Its formation is accompanied with the evolution of hydrogen, and is founded upon the property which cobalt has of oxidising in an alkaline solution, the development of which has been observed in such a considerable measure in the cobaltamine salts. The process which goes on here may be expressed by the following equation: $CoC_2N_2 + 4KCN$ first forms $CoK_4C_6N_6$, which salt with water, H_2O, forms potassium hydroxide, KHO, hydrogen, H, and the salt $K_3CoC_6N_6$. Here naturally the presence of the acid is indispensable in consequence of its being required to combine with the alkali. From aqueous solutions this salt crystallises in transparent, hexagonal prisms of a yellow colour, easily soluble in water. The reactions of double decomposition, and even the formation of the corresponding acid, are here completely the same as in the case of the ferricyanide. If a nickelous salt be treated in precisely the same manner as has just been described for a salt of cobalt, decomposition will occur.

hydroxide be shaken in water and chlorine gas be passed through it, then nickel chloride will be formed, which is soluble in water, and insoluble nickelic oxide in the form of a black precipitate: $3NiH_2O_2 + Cl_2 = NiCl_2 + Ni_2O_3, 3H_2O$. Nickelic oxide may also be obtained by adding sodium hypochlorite mixed with alkali to a solution of a nickel salt. Nickelic and cobaltic oxides (hydrated) have a black colour and exhibit but slight tendency to combine with acids, nickelic oxide up to the present time not having been combined with any acid, so that it corresponds in properties with manganese dioxide. It actually evolves oxygen with all acids, and in consequence of this it is not separated as a precipitate in the presence of acids; thus it evolves chlorine with hydrochloric acid, exactly like manganese dioxide. When nickelic oxide is dissolved in aqueous ammonia it disengages nitrogen, and an ammoniacal solution of nickelous oxide is formed. When heated nickelic oxide loses oxygen, forming nickelous oxide. Cobaltic oxide, Co_2O_3, exhibits more stability than nickelic oxide, and shows feeble basic properties; thus it is dissolved in acetic acid without the evolution of oxygen. But ordinary acids, especially when heated, evolve oxygen, forming a solution of a cobaltous salt. The presence of a cobaltic salt in a solution of a cobaltous salt may be detected by the brown colour of the solution and the black precipitate formed by the addition of alkali, and also from the fact that such solutions evolve chlorine when heated with hydrochloric acid. Cobaltic oxide may not only be prepared by the above-mentioned methods, but also by heating cobalt nitrate, after which a steel-coloured mass remains which retains certain traces of nitric acid, but when heated to incandescence it evolves oxygen, leaving a compound of cobaltic and cobaltous oxides, similar to magnetic ironstone.

Nickel alloys possess qualities which render them valuable in industry, the alloy of nickel with iron being particularly remarkable. This alloy is met with in nature as *meteoric iron*. The Pallasoffsky mass of meteoric iron, preserved in the St. Petersburg Academy, fell in Siberia in the last century; it weighs about 15 cwt. and contains 88 p.c. of iron and about 10 p.c. of nickel, with a small admixture of other metals. In the arts *German silver* is the most extensively used; it is an alloy containing nickel, copper, and zinc in various proportions. It generally consists of about 50 parts of copper, 25 parts of zinc, and 25 parts of nickel. This alloy is characterised by its white colour resembling that of silver, and, like this latter metal, it does not rust, and therefore furnishes an excellent substitute for silver in the majority of cases where it is used. Alloys which contain silver in addition to nickel show the properties of silver to a still greater extent.

Alloys of nickel are used for currency, and if rich deposits of nickel are discovered a wide field of application lies before them, both in a pure state (because it is a beautiful metal and does not rust) and also as alloys. Steel vessels (pressed or forged out of sheet steel) covered with nickel have such practical merits that the manufacture, which has not long commenced, will most probably be rapidly developed.

CHAPTER XXIII

THE PLATINUM METALS

THE six metals: Ruthenium, Ru, rhodium, Rh, palladium, Pd, osmium, Os, iridium, Ir, and platinum, Pt, are met with associated together in nature. Platinum always predominates over the others, and hence they are known as the *platinum metals*. By their chemical character their position in the periodic system is in the eighth group, corresponding with iron, cobalt, and nickel.

The naturalness of the transition from titanium and vanadium to copper and zinc by means of the elements of the iron group is demonstrated by all the properties of these elements, and in exactly the same manner a transition from zirconium, niobium, and molybdenum to silver, cadmium, and indium, through ruthenium, rhodium, and palladium is in perfect accordance with fact, as also is the position of osmium, iridium, and platinum between tantalum and tungsten on the one side, and gold and mercury on the other. In all these three cases the elements of smaller atomic weight (chromium, molybdenum, and tungsten) are able, in their higher grades of oxidation, to give acid oxides having the properties of distinct but feebly energetic acids (in the lower oxides they give bases), whilst the elements of greater atomic weight (zinc, cadmium, mercury), even in their higher grades of oxidation, only give bases, although with feebly-developed basic properties. The platinum metals present the same intermediate properties such as we have already seen in iron and the elements of the eighth group.

In the platinum metals the intermediate properties *of feebly acid and feebly basic metals* are developed with great clearness, so that there is not one sharply-defined acid anhydride among their oxides, although there is a great diversity in the grades of oxidation from the type RO_4 to R_2O. The feebleness of the chemical forces observed in the platinum metals is connected with the ready decomposability of their compounds, with the small atomic volume of the metals themselves, and with their large atomic weight. The oxides of platinum, iridium, and osmium can scarcely be either termed basic or acid; they

are capable of combinations of both kinds, one and the other of which is feeble. They are all intermediate oxides.

The atomic weights of platinum, iridium, and osmium are nearly 191 to 196, and of palladium, rhodium, and ruthenium, 104 to 106. Thus, strictly speaking, we have here two series of metals, which are, moreover, perfectly parallel to each other; three members in the first series, and three members in the second—namely, platinum presents an analogy to palladium, iridium to rhodium, and osmium to ruthenium. The *group* of the platinum metals is characterised by *a number of common properties*, both physical and chemical, and, moreover, there are not a few points of resemblance between the members of this group and those of the *iron* group (Chapter XXII.). The atomic volumes of the elements of this group are *nearly equal* and *very small*. The iron metals have atomic volumes of nearly 7, whilst that of the metals allied to palladium is nearly 9, and of those adjacent to platinum nearly 9·4. This comparatively small atomic volume corresponds with the great infusibility and tenacity proper to all the iron and platinum metals, and to their small chemical energy, which stands out very clearly in the heavy platinum metals. All the platinum metals are very *easily reduced* by ignition and by the action of various reducing agents, in which process oxygen, or a haloid group, is disengaged from their compounds and the metal left behind. This is a property of the platinum metals which determines many of their reactions, and the circumstance of their always being found in nature *in a native state*.[1] The facility with which they are reduced is so great that their chlorides are even decomposed by gaseous hydrogen, especially when shaken up and heated under a certain pressure. Hence it will be readily understood that such metals as zinc, iron, &c., separate them from solutions with great ease, which fact is taken advantage of in practice and in the chemical treatment of the platinum metals.

All the platinum metals, like those of the iron group, are grey, with a comparatively feeble metallic lustre, and are very infusible. In this respect they stand in the same order as the metals of the iron series; nickel is more fusible and whiter than cobalt and iron, so also palladium is whiter and more fusible than rhodium and ruthenium, and platinum is comparatively more fusible and whiter than iridium or osmium. The saline compounds of these metals are red or yellow, like

[1] Wells and Penfield (1888) have described a mineral sperryllite found in the Canadian gold-bearing quartz and consisting of platinum diarsenide, $PtAs_2$. It is a noticeable fact that this mineral clearly confirms the position of platinum in the same group as iron, because it corresponds in crystalline form (regular octahedron) and chemical composition with iron pyrites, FeS_2.

those of the majority of the metals of the iron series. But here, as there, the different forms of oxidation present different colours. Moreover, certain complex compounds of the platinum metals, like certain complex compounds of the iron series, either have particular characteristic tints or else are colourless.

The platinum metals are found *in nature associated together in alluvial deposits* in a few localities, from which they are washed, owing to their very considerable density, which enables a stream of water to wash away the sand and clay with which they are mixed. Platinum deposits are chiefly known in the Urals, and also in Brazil and a few other localities. The platinum ore washed from these alluvial deposits presents the appearance of more or less coarse grains, and sometimes of, as it were, semifused nuggets.[2]

All the platinum metals give compounds with the halogens, and the highest haloid type of combination for all is RX_4. For the majority of the platinum metals this type is exceedingly unstable; the lower compounds corresponding to the type RX_2, which are formed by the separation of X_2, are more stable. In the type RX_2 the platinum metals form more stable salts, which offer no little resemblance to the kindred compounds of the iron series—for example, with nickelous chloride, $NiCl_2$, cobaltous chloride, $CoCl_2$, &c. This even expresses itself in a similarity of volume (platinous chloride, $PtCl_2$, volume, 46; nickelous chloride, $NiCl_2=50$), although in the type RX_2 the true iron metals give very stable compounds, whilst the platinum metals frequently react after the manner of suboxides, decomposing into the metal and higher types, $2RX_2=R+RX_4$. This naturally depends on the facility with which RX_2 decomposes into R and X_2, when X_2 combines with the remaining RX_2.

As in the series iron, cobalt, nickel, nickel *gives only one* salt-forming oxide, whilst cobalt and iron give higher and varied forms of oxidation; so also among the platinum metals, platinum and palladium only give the forms RX_2 and RX_4, whilst rhodium and iridium form

[2] The largest amount of platinum is extracted in the Urals, about two tons annually. About a tenth part of gold is extracted from the washed platinum by means of mercury, which does not dissolve the platinum metals but dissolves the gold accompanying the platinum in its ores. Moreover, the ores of platinum always contain metals of the iron series associated with them. The washed and mechanically-sorted ore in the majority of cases contains about 70 to 80 p.c. of platinum, about 5 to 8 p.c. of iridium, and a somewhat smaller quantity of osmium. The other platinum metals—palladium, rhodium, and ruthenium—occur in smaller proportions than the three above named. Sometimes grains of almost pure osmium-iridium, containing only a small quantity of other metals, are found in platinum ores. This osmium-iridium may be easily separated from the other platinum alloys, owing to its being nearly insoluble in aqua regia, by which the latter are easily dissolved. There are grains of platinum which are magnetic.

yet another intermediate type, RX_3, corresponding with the oxide, which is also met with for cobalt, and presents the composition R_2O_3, besides which they also form an acid oxide, like ferric acid, which is also known in the form of salts, but is in every respect unstable. *Osmium* and *ruthenium*, like manganese, form still higher oxides, and in this respect exhibit the greatest diversity. They not only give RX_2, RX_3, RX_4, and RX_6, but also a still *higher form of oxidation*, RO_4, which is not met with in any other series. This form is exceedingly characteristic, owing to the fact of the oxides, OsO_4 and RuO_4, being volatile feebly acid substances. In this respect they most resemble permanganic anhydride, which is also somewhat volatile.[3]

When dissolved in aqua regia and liberated from the solution by ignition or the action of reducing agents, platinum forms a powdery mass, known as spongy platinum or platinum black. If this powder of platinum be heated and pressed, or hammered in a cylinder, the grains

[3] In characterising the platinum metals according to their relation to the iron metals, it is very important to add two more very remarkable points. The platinum metals are capable of forming a sort of unstable compound with *hydrogen*; they absorb it and only part with it when somewhat considerably heated. This faculty is especially developed in platinum and palladium, and it is very characteristic that nickel, which just corresponds with platinum and palladium in the periodic system, should exhibit the same faculty for retaining a considerable quantity of hydrogen (Graham's and Raoult's experiments). Another characteristic property of the platinum metals consists in their easily giving stable and characteristic saline *compounds with ammonia*, and double salts with the cyanides of the alkali metals, especially in their lower forms of combination.

All the above so clearly brings the elements of the iron series in close relation to the platinum metals, that the eighth group acquires as natural a character as can be required, with a certain originality or individuality for each element.

Platinum was first obtained in the last century from Brazil, where it was called silver (platinus). Watson in 1750 characterised platinum as a separate independent metal. In 1803 Wollaston discovered palladium and rhodium in crude platinum, and at about the same time Tennant distinguished iridium and osmium in it. Professor Claus, of Kazan, in his researches on the platinum metals (about 1840) discovered ruthenium in them, and to him are due many important discoveries with regard to these elements, such as the indication of the remarkable analogy between the series Pd—Rh—Ru and Pt—Ir—Os.

The treatment of platinum ore is chiefly carried on for the extraction of the platinum itself and its alloys with iridium, because these metals offer a greater resistance to the action of chemical reagents and high temperatures than any of the other malleable and ductile metals, and therefore the wire so often used in the laboratory and for technical purposes is made from them, as also are various vessels used for chemical purposes in the laboratory and in works. Thus sulphuric acid is distilled in platinum retorts, and many substances are fused, ignited, and evaporated in the laboratory in platinum crucibles and platinum foil. Gold and many other substances are dissolved in basins made of iridium-platinum, because the alloys of platinum and iridium are but slightly attacked when subjected to the action of aqua regia. An exceedingly important property of the platinum metals is that they do not fuse in a furnace heat, palladium only being somewhat more fusible than the rest.

aggregate or forge together, and form a continuous, but naturally not entirely homogeneous, mass. Platinum was formerly, and is even now, worked up in this manner. The platinum money formerly used in Russia was made in this way. Sainte-Claire Deville, in the fifties, for the first time *melted platinum* in considerable quantities by employing a special furnace made in the form of a small reverberatory furnace, and composed of two pieces of lime, on which heat has no action. Into this furnace (shown in fig. 34, Vol. I. p. 173)—or, more strictly speaking, into the cavity made in the pieces of lime—the platinum is introduced, and two orifices are made in the lime; through one, the upper, or side orifice, is introduced an oxyhydrogen gas burner, in which either detonating gas or a mixture of oxygen and coal-gas is burnt, whilst the other orifice serves for the escape of the products of combustion and certain impurities which are more volatile than the platinum, and especially the oxidised compounds of osmium, ruthenium, and palladium, which are comparatively easily volatilised by heat. In this manner the platinum is converted into a continuous metallic form by means of fusion, and this method is now used for melting somewhat considerable masses of platinum.[4]

If it be desired to obtain pure platinum, it is necessary to have recourse to the solution of the ore in aqua regia. Only the osmium and iridium remain unattacked by the aqua regia. The solution contains the platinum metals in the form RCl_4, and in the lower forms of chlorination, because some of these metals—for instance, palladium and rhodium—form such unstable chlorides of the type RX_4 that they already partially decompose when only diluted with water, and pass into the stable lower type of combination; in addition to which the chlorine is very easily disengaged if it comes in contact with substances on which it can act. In this respect platinum resists the action of

[4] This process has altered the technical treatment of platinum to a considerable extent. It has in particular facilitated the manufacture of alloys of platinum with iridium and rhodium from the pure platinum ores; because it is sufficient to fuse the ore in order for the greater amount of the osmium to burn off, and for the mass to fuse into a homogeneous, malleable alloy, which is straightway used in practice. There is very little ruthenium in the ores of platinum. If during fusion lead be added, it dissolves the platinum owing to its being able to form a very characteristic alloy containing PtPb. If an alloy of both metals be left exposed to moist air, the excess of lead is converted into carbonate (white lead) in the presence of the water and carbonic acid of the air, whilst the above platinum alloy remains unchanged. The white lead may be extracted by dilute acid, and the alloy PtPb remains untouched. The other platinum metals also give similar alloys with lead. The fusibility of these alloys enables the platinum metals to be separated from the gangue of the ore, and they may afterwards be separated from the lead by subjecting the alloy to oxidation in furnaces furnished with a bone ash bed, because the lead is then oxidised and absorbed by the bone ash, leaving the platinum metals untouched.

heat and reducing agents better than any of its companions—that is, it passes with greater difficulty from $PtCl_4$ to the lower compound $PtCl_2$. On this is based the method of preparation of more or less pure platinum. Lime or sodium hydroxide is added to the solution in aqua regia; in one or the other case the reaction is not carried on to the formation of a clearly alkaline solution, but only to saturation or a very slight excess of alkali. It is naturally best to first evaporate and slightly ignite the solution, in order to remove the excess of acid, and by heating it to partially convert the higher chlorides of the palladium, &c., into the lower. The addition of alkalis completes the reduction, because the chlorine held in the compounds RX_4 acts on the alkali like free chlorine, converting it into a hypochlorite. Thus palladium chloride, $PdCl_4$, for example, is converted into palladious chloride, $PdCl_2$, by this means, according to the equation $PdCl_4 + 2NaHO = PdCl_2 + NaCl + NaClO + H_2O$. In just the same manner iridic chloride, $IrCl_4$, is converted into the trichloride, $IrCl_3$, by this method. When this conversion takes place the platinum still remains in the form of platinic chloride, $PtCl_4$. It is then possible to take advantage of a certain difference in the properties of the higher and lower chlorides of the platinum metals. Thus lime precipitates the lower chlorides of the members of the platinum metals occurring in solution without acting on the platinic chloride, $PtCl_4$, and therefore the addition of a large proportion of lime immediately precipitates the associated metals, leaving the platinum itself in solution in the form of a soluble double salt, $PtCl_4,CaCl_2$. A far better and more perfect *separation* is effected *by means of ammonium chloride*, which gives, with platinic chloride, an insoluble yellow precipitate, $PtCl_4,2NH_4Cl$, whilst it forms soluble double salts with the lower chlorides RCl_2 and RCl_3, so that ammonium chloride precipitates the platinum only from the solution obtained by the preceding method. These methods are employed for preparing the platinum which is used for the manufacture of platinum articles, because, having platinum in solution as calcium platinochloride, $PtCaCl_6$, or as the insoluble ammonium platinochloride, $Pt(NH_4)_2Cl_6$, the platinum compound in every case, after drying or ignition, loses all the chlorine from the platinic chloride and leaves finely-divided metallic platinum, which may be converted into homogeneous metal by compression and forging, or by fusion.[5]

[5] For the ultimate purification of platinum from palladium and iridium the metals must be re-dissolved in aqua regia, and the solution evaporated until the residue begins to evolve chlorine. The residue is then re-precipitated with ammonium or potassium chloride. The precipitate may still contain a certain amount of iridium, which passes with greater difficulty from the tetrachloride, $IrCl_4$, into the trichloride, $IrCl_3$, but it will

Metallic *platinum* in a fused state has a specific gravity of 21·1 ; it is grey, softer than iron, but harder than copper, exceedingly ductile, and therefore is easily drawn into wire and rolled into thin sheets, and may be hammered and drawn into thin tubes, &c. In the state in which it is obtained by the ignition of its compounds, it forms a spongy mass, known as spongy plantinum, or else as powder (platinum black).[6] In either case it is grey, dull, and is characterised, as we already know, by the faculty of absorbing hydrogen and other gases. Platinum is not acted on by hydrochloric, hydriodic, nitric, and sulphuric acids, or a mixture of hydrofluoric and nitric acids. Aqua regia, and any liquid containing chlorine or able to evolve chlorine or bromine, dissolves platinum. Alkalis are decomposed by platinum at a red heat, owing to the faculty of the platinum oxide, PtO_2, formed to combine with alkaline bases, inasmuch as it has a feebly-developed acid character. Sulphur, phosphorus (the phosphide, PtP_2, is formed), arsenic, silicon all act more or less rapidly on platinum, under the influence of heat. Many of the metals form alloys with it. Even charcoal combines with platinum when it is ignited with it, and therefore carbonaceous matter cannot be subjected to prolonged and powerful ignition in platinum vessels. Hence a platinum crucible soon becomes dull on the surface in a smoky flame. Platinum also alloys with zinc, lead, tin, copper, gold, and silver.[7] Although mercury does

be quite free from palladium, because the latter easily loses its chlorine and passes into palladious chloride, $PdCl_2$, which gives an easily-soluble salt with potassium chloride. The precipitate, containing a small quantity of iridium, is then heated, with sodium carbonate, in a crucible, when the mass decomposes, giving metallic platinum and iridium oxide. If potassium chloride has been employed, the residue after ignition is washed with water and treated with aqua regia. The iridium oxide remains undissolved, and the platinum easily passes into solution. Only cold and dilute aqua regia must be used. The solution will then contain pure platinic chloride, which forms the starting-point for the preparation of all platinum compounds.

[6] We have already become acquainted with the effect of finely-divided platinum on many gaseous substances. It is best seen in the so-called *platinum black*, which is a coal black powder left by the action of sulphuric acid on the alloy of zinc and platinum, or which is precipitated by metallic zinc from a dilute solution of platinum. At all events, finely-divided platinum absorbs gases more powerfully and rapidly the more finely-divided and porous it is. Sulphurous anhydride, hydrogen, alcohol, and many organic substances in the presence of such platinum are easily oxidised by the oxygen of the air, although they do not combine with it directly. The absorption of oxygen is as much as several hundred volumes per one volume of platinum, and the oxidising power of such absorbed oxygen is taken advantage of not only in the laboratory but even in working processes. Asbestos or charcoal, soaked in a solution of platinic chloride and ignited, is very useful for this purpose, because by this means it becomes coated with platinum black.

[7] It is necessary to remark that platinum when alloyed with silver, or as amalgam, is soluble in nitric acid, and in this respect it differs from gold, so that it is possible by alloying gold with silver and acting on the alloy with nitric acid, to recognise the presence of platinum in the gold, because nitric acid does not act on gold alloyed with silver.

not directly dissolve platinum, still it forms a solution or amalgam with spongy platinum, in the presence of sodium amalgam; a similar amalgam is also formed by the action of sodium amalgam on a solution of platinum chloride, and is used for physical experiments.

There are *two kinds* of *platinum compounds*, PtX_4 and PtX_2. The former are produced by an excess of halogen in the cold, and the latter by the aid of heat or by the splitting up of the former. The starting-point of the platinum compounds is *platinum tetrachloride, platinic chloride*, $PtCl_4$, obtained by dissolving platinum in aqua regia. The solution crystallises in the cold, in a desiccator, in the form of reddish-brown deliquescent crystals containing hydrochloric acid: $PtCl_4,2HCl,6H_2O$, and forming a true acid with corresponding salts R_2PtCl_6—ammonium platinochloride, for example. The hydrochloric acid is liberated from these crystals by gently heating or evaporating the solution to dryness; and, better still, after treatment with silver nitrate (silver chloride is precipitated) a reddish-brown mass remains behind, which dissolves in water, and forms a yellowish-red solution which on cooling deposits crystals of the composition $PtCl_4,8H_2O$. The *tendency to combine* with hydrochloric acid and water—that is, *to form higher crystalline compounds*—is evident in the platinum compounds, and must be taken into account in explaining the properties of platinum and the formation of many other of its complex compounds. Dilute solutions of platinic chloride are yellow, and are completely reduced by hydrogen, sulphurous anhydride, and many reducing agents, which first convert the platinic chloride into the lower compound platinous chloride, $PtCl_2$. That faculty which expresses itself in platinum tetrachloride in its combining with water of crystallisation and hydrochloric acid is distinctly marked in its property, with which we are already acquainted, of giving precipitates with the salts of potassium, ammonium, rubidium, &c. In general it *readily forms double salts* $R_2PtCl_6 = PtCl_4 + 2RCl$, where R is a univalent metal such as potassium or sodium. Hence the addition of a solution of potassium or ammonium chloride to a solution of platinic chloride is followed by the formation of a yellow precipitate, which is sparingly soluble in water and almost entirely insoluble in alcohol and ether (platinic chloride is soluble in water, and potassium iridiochloride, IrK_3Cl_6, is soluble in water but not in alcohol). It is especially remarkable in this case, that the potassium compounds here, as in a number of other instances, separate in an anhydrous form, whilst the sodium compounds, which are soluble in water and alcohol, form red crystals containing water. The composition $Na_2PtCl_6,6H_2O$ exactly corresponds with the above

mentioned hydrochloric compound. The compounds with barium, $BaPtCl_6,4H_2O$, strontium, $SrPtCl_6,8H_2O$, calcium, magnesium, iron, manganese, and many other metals are all soluble in water.[8]

Platinous chloride, $PtCl_2$, is formed when hydrogen platinochloride, PtH_2Cl_6, is ignited at 300°, or when platinum is heated at 230° in a stream of chlorine. The undecomposed tetrachloride is extracted from the residue by washing it with water, and a greenish grey or brown insoluble mass of the dichloride (sp. gr. 5·9) is then obtained. It is soluble in hydrochloric acid, giving an acid solution of the composition $PtCl_2,2HCl$, corresponding with the type of double salts PtR_2Cl_4. Although platinous chloride decomposes below 500°, still it is partially formed at higher temperatures. Troost and Hautefeuille, and Seelheim observed that when platinum is strongly ignited in a stream of

[8] Nilson (1877), who investigated the platinochlorides of various metals subsequently to Bonsdorff, Topsoë, Cleve, Marignac, and others, found that univalent and bivalent metals—such as hydrogen, potassium, ammonium . . . beryllium, calcium, barium—give compounds of such a composition that there is always twice as much chlorine in the platinic chloride as in the combined metallic chloride; for example, $K_2Cl_2,PtCl_4$; $BeCl_2,PtCl_4,8H_2O$, &c. Such trivalent metals as aluminium, iron (ferric), chromium, didymium, cerium (cerous) form compounds of the type RCl_3PtCl_4, in which the amounts of chlorine are in the ratio 3 : 4. Only indium and yttrium give salts of a different composition—namely, $2InCl_3,5PtCl_4,36H_2O$ and $4YCl_3,5PtCl_4,51H_2O$. Such quadrivalent metals as thorium, tin, zirconium give compounds of the type $RCl_4,PtCl_4$, in which the ratio of the chlorine = 1 : 1. In this manner the valency of a metal may, to a certain extent, be judged from the composition of the double salts formed with platinic chloride. Many of the above-mentioned compounds are, moreover, able to combine with different amounts of water of crystallisation.

Platinic bromide, $PtBr_4$, and iodide, PtI_4, are analogous to the tetrachloride, but the iodide is decomposed still more easily than the chloride. If sulphuric acid be added to platinic chloride, and the solution evaporated, it forms a black porous mass like charcoal, which deliquesces in the air, and presents the composition $Pt(SO_4)_2$. But this, the only oxygen salt of the type PtX_4, is exceedingly unstable. This is due to the fact that *platinum oxide*, the oxide of the type PtO_2, has a feeble acid character. This is shown in a number of instances. Thus if a solution of sodium carbonate be added to a strong solution of platinic chloride, and the solution be exposed to the action of light or evaporated to dryness and then washed with water, there remains a sodium platinate, $Pt_3Na_2O_7,6H_2O$. The composition of this salt, if regarded in the same sense as we did the salts of silicic, titanic, molybdic, and other acids, will be $PtO(ONa)_2,2PtO_2,6H_2O$—that is, the same type is repeated as we saw in the crystalline compounds of platinum tetrachloride with sodium chloride, or with hydrochloric acid—namely, the type $PtX_4 8Y$, where Y is the molecule H_2O,HCl, &c. Similar compounds are also obtained with other alkalis. They will be platinates of the alkalis in which the platinic oxide, PtO_2, plays the part of an acid oxide. If such an alkaline compound of platinum be treated with acetic acid, the alkali will pass over to the latter, and there remains a *platinic hydroxide*, $Pt(OH)_4$, as a brown mass, which loses water and oxygen when ignited, and in so doing decomposes with a slight explosion. When slightly ignited this hydroxide first loses water and gives the very unstable oxide PtO_2. Platinic sulphide, PtS_2, belongs to the same type; it is precipitated by the action of sulphuretted hydrogen on a solution of platinum tetrachloride. The moist precipitate is capable of attracting oxygen, and is then converted into the sulphate above mentioned, which is soluble in water. Platinic sulphide gives crystalline compounds with the alkali sulphides.

chlorine, the metal, as it were, slowly volatilised and was deposited in crystals; a volatile chloride, probably platinous chloride, was naturally formed in this case, and decomposed subsequently to its formation with the deposition of crystals of platinum.

The above-described properties of platinum are repeated, sometimes distinctly and sometimes with a certain modification, in the above-mentioned associates and analogues of this metal, but naturally there are certain points of difference.[9] With respect to the types of combi-

[9] In comparing the characteristics of the platinum metals, it is not unimportant to remark that palladium in its forms of combination PdX_2 gives saline compounds of considerable stability. Amongst them *palladous chloride* is formed by the direct action of chlorine or aqua regia (not in excess nor in dilute solutions) on palladium. It forms a brown solution, which gives a black insoluble precipitate of *palladous iodide*, PdI_2, with solutions of iodides (in this respect, as in many others, palladium resembles mercury in the mercuric compounds HgX_2). With a solution of mercuric cyanide it gives a yellowish white precipitate, palladous cyanide, PdC_2N_2, which is soluble in potassium cyanide, and gives other double salts, $M_2PdC_4N_4$.

That portion of the platinum ore which dissolves in aqua regia and is precipitated by ammonium or potassium chloride does not contain palladium. It remains in solution, because the palladic chloride, $PdCl_4$, is decomposed and the palladous chloride formed is not precipitated by ammonium chloride; the same holds good for all the other lower chlorides of the platinum metals. Zinc (and iron) separates out all the unprecipitated platinum metals (and also copper, &c.) from the solution. It is in these platinum residues precipitated by zinc that the palladium is found. If this mixture of metals is treated with aqua regia, then all the palladium will pass into solution as palladous chloride and some platinic chloride. By this treatment the main portion of the iridium, rhodium, &c., remains almost undissolved, and the platinum is separated from the mixture of palladous and platinic chlorides by a solution of ammonium chloride, and the solution of palladium is precipitated by potassium iodide or mercuric cyanide. Wilm (1881) showed that palladium may be separated from an impure solution by saturating it with ammonia; all the iron present is thus precipitated, and, after filtering, the addition of hydrochloric acid to the filtrate gives a yellow precipitate of an ammonio-palladium compound: $PdCl_2,2NH_3$, whilst nearly all the other metals remain in solution. *Metallic palladium* is obtained by igniting the ammonio-compound or the cyanide, PdC_2N_2. It occurs native, although rarely, and is a metal of a whiter colour than platinum, sp. gr. 11·8; it is much more fusible than platinum, partially oxidises on the surface when heated, and loses its absorbed oxygen on a further rise of temperature. It does not blacken or tarnish (does not absorb sulphur) in the air at the ordinary temperature, and is therefore better suited than silver for astronomical and other instruments in which fine divisions have to be engraved on a white metal, in order that the fine lines should be clearly visible. The most remarkable property of palladium, discovered by Graham, consists in its capacity for *absorbing* a large amount of *hydrogen*. Ignited palladium absorbs as much as 940 volumes of hydrogen, or about 0·7 p.c. of its own weight, which closely approaches to the formation of the compound Pd_5H_2, and probably corresponds with the formation of *palladium hydride*, Pd_2H. This absorption also takes place at the ordinary temperature—for example, when palladium serves as an electrode on which hydrogen is evolved. In absorbing the hydrogen, the palladium does not change in appearance, and retains all its metallic properties, only its volume increases by about 10 p.c.—that is, the hydrogen pushes out and separates the atoms of the palladium from each other, and is itself compressed to $\frac{1}{600}$ of its volume. This compression indicates a great force of chemical attraction, and is accompanied by the evolution of heat (Vol. I. p. 141 and p. 599, Note 44). The absorbed hydrogen is easily disengaged

nation, all the platinum metals, as was said above, under the action of by ignition or decreased pressure. The resultant compound does not decompose at the ordinary temperature, but when exposed to air the metal sometimes glows spontaneously, owing to the hydrogen burning at the expense of the atmospheric oxygen. The hydrogen absorbed by palladium acts towards many solutions as a reducing agent; in a word, everything here points to the formation of a definite compound and at the same time of a physically-compressed gas, and forms one of the best examples of the bond existing between chemical and physical processes, to which we have many times drawn attention. It must be again remembered that the other metals of the eighth group, even copper, are, like palladium and platinum, able to combine with hydrogen. The permeability of iron and platinum tubes to hydrogen is naturally due to the formation of similar compounds, because palladium is the most permeable.

Rhodium is generally separated, together with iridium, from the residues left after the treatment of native platinum, because the palladium is entirely separated from them, and the ruthenium is present in them in very small traces, whilst the osmium at any rate is easily separated, as we shall soon see. The mixture of rhodium and iridium which is left undissolved in dilute aqua regia is dissolved in chlorine water, or by the action of chlorine on a mixture of the metals with sodium chloride. In either case both metals pass into solution. They may be separated by many methods. In either case (if the action be aided by heat) the rhodium is obtained in the form of the chloride $RhCl_3$, and the iridium as iridious chloride, $IrCl_3$. They both form double salts with sodium chloride which are soluble in water, but the iridium salt is also partially soluble in alcohol, whilst the rhodium salt is not. A mixture of the chlorides, when treated with dilute aqua regia, gives iridic chloride, $IrCl_4$, whilst the rhodium chloride, $RhCl_3$, remains unaltered; ammonium chloride then precipitates the iridium as ammonium iridiochloride, $Ir(NH_4)_2Cl_6$, and on evaporating the rose-coloured filtrate the rhodium gives a crystalline salt, $Rh(NH_4)_3Cl_6$. Rhodium and its various oxides are dissolved when fused with potassium hydrogen sulphate, and give a soluble double sulphate (whilst iridium remains unacted on); this fact is very characteristic for this metal, which offers many points of resemblance with the iron metals in its properties. When fused with potassium hydroxide and chlorate it, like iridium, is oxidised, but it is not afterwards soluble in water, in which it differs from ruthenium. This is taken advantage of for separating rhodium, ruthenium, and iridium. In any case, rhodium under ordinary conditions always gives salts of the type RX_3, and not of any other type; and not only halogen salts, but also oxygen salts, are known in this type, which is rare among the platinum metals. Rhodium chloride, $RhCl_3$, is known in an insoluble anhydrous and also in a soluble form, in which it easily gives double salts, compounds with water of crystallisation, and forms rose-coloured solutions. In this form rhodium easily gives double salts of the two types RhM_3Cl_6 and RhM_2Cl_5—for example, $K_3RhCl_6,3H_2O$ and K_2RhCl_5,H_2O. Solutions of the salts (at least, the ammonium salt) of the first kind give salts of the second kind when they are boiled. If a strong solution of potash is added to a red solution of rhodium chloride and boiled, a black precipitate of the hydroxide $Rh(OH)_3$ is formed; but if the solution of potash is added little by little, it gives a yellow precipitate containing more water. This yellow hydrate of rhodium oxide gives a yellow solution when it is dissolved in acids, which only becomes rose-coloured after being boiled. It is obvious that some, as yet unknown, change here takes place, like the transmutations of the salts of chromic oxide. It is also a remarkable fact that the black hydroxide, like many other oxidised compounds of the platinoid metals, does not dissolve in the ordinary oxygen acids, whilst the yellow hydroxide is easily soluble and gives yellow solutions, which deposit imperfectly crystallised salts. Metallic rhodium is easily obtained by igniting its oxygen and other compounds in hydrogen, or by precipitation with zinc. It resembles platinum, and has a sp. gr. of 12·1. At the ordinary temperature it decomposes formic acid into hydrogen and carbonic anhydride, with development of heat (Deville). With the alkali sulphites, the salts of rhodium and iridium of the type RX_3 give sparingly-soluble precipitates of double sulphites of the

an excess of chlorine or of oxdising agents give compounds of the type

composition $R(SO_3Na)_3,H_2O$, by means of which these metals may be separated from solution, and also may be separated from each other, for a mixture of these salts when treated with strong sulphuric acid gives a soluble iridium sulphate and leaves a red insoluble double salt of rhodium and sodium. It is further necessary to remark that the oxides Ir_2O_3 and Rh_2O_3 are comparatively stable and are very often formed. Thus the *iridious oxide*, Ir_2O_3, is obtained by fusing iridious chloride and its compounds with sodium carbonate, and treating the mass with water. The oxide is then left as a black powder, which, when strongly heated, is decomposed into iridium and oxygen; it is easily reduced, and is insoluble in acids, which indicates the feeble basic character of this oxide, in many respects resembling such oxides as cobaltic oxide, ceric or lead dioxide, &c. It does not dissolve when fused with potassium hydrogen sulphate. Rhodium oxide, Rh_2O_3, is a far more energetic base. It dissolves when fused with potassium hydrogen sulphate.

From what has been said respecting the separation of platinum and rhodium it will be understood how the compounds of *iridium*, which is the main associate of platinum, are obtained. In describing the treatment of osmiridium we shall again have an occasion of learning the method of extraction of the compounds of this metal, which has in recent times found a technical application in the form of its oxide, Ir_2O_3; this is obtained from many of the compounds of iridium by ignition with water, and is easily reduced by hydrogen and is insoluble in acids. It is used in painting on china, for giving a black colour. Iridium itself is more difficultly fusible than platinum, and when fused it does not decompose acids or even aqua regia; it is extremely hard, and is not malleable; its sp. gr. is 21·1. In the form of powder it dissolves in aqua regia, and is even partially oxidised when heated in air, sets fire to hydrogen, and, in a word, closely resembles platinum. Heated in an excess of chlorine it gives iridic chloride, $IrCl_4$, but this loses chlorine at 50°; it is, however, more stable in the form of double salts, but they give iridious chloride, $IrCl_3$, when treated with sulphuric acid.

We have yet to become acquainted with the two remaining associates of platinum—ruthenium and osmium—whose most important property is that they are oxidised even when heated in air, and that they are able to give *volatile* oxides of the form RuO_4 and OsO_4; these have a powerful odour (like iodine and nitrous anhydride). Both these higher oxides are solids; they volatilise with great ease at 100°; the former is yellow and the latter white. They are known as *ruthenic* and *osmic anhydrides*, although their aqueous solutions (they both slowly dissolve in water) do not show an acid reaction, and although they do not even expel carbonic anhydride from potassium carbonate, do not give crystalline salts with bases, and their alkaline solutions partially deposit them again when boiled (an excess of water decomposes the salts). The formulæ OsO_4 and RuO_4 correspond with the vapour density of these oxides. Thus Deville found the vapour density of osmic anhydride to be 128 (by the formula 127·5) referred to hydrogen. Tennant and Vauquelin discovered this compound, and Berzelius, Wöhler, Fritzsche, Struvé, Deville, Claus, and others helped in its investigation; nevertheless there are still many questions concerning it which remain unsolved. It should be observed that RO_4 is the highest known form for an oxygen compound, and RH_4 is the highest known form for a compound of hydrogen; and the highest forms of acid hydrates contain SiH_4O_4, PH_3O_4, SH_2O_4, $ClHO_4$—all with four atoms of oxygen, and therefore in this number there is apparently the limit for the simple forms of combination of hydrogen and oxygen. For *several* atoms of an element or for several elements there may be more than O_4 or H_4, but a molecule never contains more to one atom of another element. Thus the simplest forms of combination of hydrogen and oxygen are exhausted by the list RH_4, RH_3, RH_2, RH, RO, RO_2, RO_3, RO_4. The extreme members are RH_4 and RO_4, and are only met with for such elements as carbon, silicon, osmium, ruthenium, which also give RCl_4 with chlorine. In these extreme forms, RH_4 and RO_4, the compounds are the least stable (compare SiH_4, PH_3, SH_2, ClH, or RuO_4, MoO_3, ZrO_2, SrO), and easily give up part, or even all, their oxygen or hydrogen.

The primary source from which the compounds of ruthenium and osmium are

RX_4—for instance, RO_2, RCl_4, &c. This is the highest form for

obtained is either *osmiridium* (the osmium predominates, from IrOs to $IrOs_4$, sp. gr. from 16 to 21), which occurs in platinum ores (it is distinguished from the grains of platinum by its crystalline structure, hardness, and insolubility in aqua regia), or else those insoluble residues which are obtained, as we saw above, after treating platinum with aqua regia. Osmium predominates in these materials, which sometimes contain from 30 p.c. to 40 p.c. of it, and rarely more than 4 p.c. to 5 p.c. of ruthenium. The process for their treatment is as follows: they are first fused with 6 parts of zinc, and the zinc then extracted with dilute hydrochloric acid. The osmiridium thus treated is, according to Fritzsche and Struvé's method, then added to a fused mixture of potassium hydroxide and chlorate in an iron crucible; the mass as it begins to evolve oxygen acts on the metal, and the reaction afterwards goes on unaided. The dark product is treated with water, and gives a solution of osmium and ruthenium in the form of soluble salts R_2OsO_4 and R_2RuO_4, whilst the insoluble residue contains a mixture of oxides of iridium (and some osmium, rhodium, and ruthenium), and grains of metallic iridium still unacted on. According to Fritzsche's method the lumps of osmiridium are straightway heated to whiteness in a porcelain tube in a stream of air or oxygen, when the very volatile osmic anhydride is obtained directly, and is collected in a well-cooled receiver, while the ruthenium gives a crystalline sublimate of the dioxide, RuO_2, which is, however, very difficultly volatile (it volatilises together with osmic anhydride), and therefore remains in the cooler portions of the tube; this method does not give volatile ruthenic anhydride, and the iridium and other metals are not oxidised or give non-volatile products. This method is simple, and at once gives dry, pure osmic anhydride in the receiver, and ruthenium dioxide in the sublimate. The air which passes through the tube should be previously passed through sulphuric acid, not only for the sake of drying, but also to remove the organic and reducing dust. The vapour of osmic anhydride must be powerfully cooled, and ultimately passed over caustic potash. A third mode of treatment, which is most frequently employed, was proposed by Wöhler, and consists in slightly heating (in order that the sodium chloride should not volatilise) an intimate mixture of osmiridium and common salt in a stream of moist (undried) chlorine. The metals then form compounds with chlorine and sodium chloride, whilst the osmium forms the chloride, $OsCl_4$, which reacts with the moisture, and gives osmic anhydride, which is condensed. The ruthenium in this, as in the other processes, does not directly give ruthenic anhydride, but is always extracted as the soluble ruthenium salt, K_2RuO_4, obtained by fusion with potassium hydroxide and chlorate or nitrate. When the orange-coloured ruthenate, K_2RuO_4, is mixed with acids the liberated ruthenic acid immediately decomposes into the volatile ruthenic anhydride and the insoluble ruthenic oxide: $2K_2RuO_4 + 4HNO_3 = RuO_4 + RuO_2, 2H_2O + 4KNO_3$. When once one of the above compounds of ruthenium or osmium is procured it is easy to obtain all the remaining compounds, and by reduction (by metals, hydrogen, formic acid, &c.) the metals themselves.

Osmic anhydride, OsO_4, is very easily deoxidised by many methods. It blackens organic substances, owing to reduction, and is therefore used in investigating vegetable and animal, and especially nerve, preparations under the microscope. Although osmic anhydride may be distilled in hydrogen, still complete reduction is accomplished when a mixture of hydrogen and osmic anhydride is slightly ignited (just before it inflames). If osmium be placed in the flame it is oxidised, and gives vapours of osmic anhydride, which are reduced, and the flame gives a brilliant light. Osmic anhydride deflagrates like nitre on red-hot charcoal; zinc, and even mercury and silver, reduce osmic anhydride from its aqueous solutions into the lower oxides or metal; such reducing agents as hydrogen sulphide, ferrous sulphate, or sulphurous anhydride, alcohol, &c., act in the same manner with great ease.

The lower oxides of osmium, ruthenium, and of the other elements of the platinum series are not volatile, and it is very worthy of remark that the other elements present a different phenomenon. On comparing SO_2, SO_3; As_2O_3, As_2O_5; P_2O_3, P_2O_5; CO, CO_2, &c., we observe a converse phenomenon; the higher oxides are less volatile than the

platinum and palladium.[10] The remaining platinum metals further, *like iron, give acids* of the type RO_3, or, more correctly, H_2RO_4=

lower. In the case of osmium all the oxides, with the exception of the highest, are non-volatile, and it may therefore be thought that this higher form is more simply constituted than the lower. Perhaps osmic oxide, OsO_2, stands in the same relation to the anhydride as C_2H_4 to CH_4—*i.e.*, perhaps the lower oxide is Os_2O_4, or presents a still higher polymerism, and it will then be understood how the lower oxides, having a greater molecular weight, are less volatile than the higher oxides, just as we saw in the case of the nitrogen oxides, N_2O and NO.

Ruthenium and osmium, obtained by the ignition or reduction of their compounds in a form of powder, have a density considerably less than in the fused form, and differ in this form in their capacity for reaction; they are much more difficultly fused than platinum and iridium, although ruthenium is more fusible than osmium. The powder of ruthenium has a specific gravity of 8·5, the fused metal of 11·4; osmium in powder has a specific gravity of 20·0, and when semi-fused—or, more strictly speaking, agglomerated—in the oxy-hydrogen flame, of 21·4. The powder of slightly-heated osmium oxidises very easily in the air, and when ignited burns like tinder, directly forming the odoriferous (hence its name, from the Greek word signifying odour) osmic anhydride; ruthenium also oxidises when heated in air, but with more difficulty, forming the oxide RuO_2. The oxides of the types RO, R_2O_3, and RO_2 (and their hydrates), obtained by reduction from the higher oxides, and also from chlorides, are analogous to those given by the other platinum metals, in which respect osmium and ruthenium closely resemble them. We may also remark that ruthenium has been found in the platinum deposits of Borneo in the form of *laurite*, R_2S_3, in grey octahedra of sp. gr. 7·0.

Debray and Joly showed that ruthenic anhydride, RuO_4, fuses at 25°, boils at 100°, and evolves oxygen when dissolved in potash, forming the salt $KRuO_4$ (not isomorphous with potassium permanganate).

[10] Although palladium gives the same types of combination (with chlorine) as platinum, its reduction is incomparably easier than that of platinic chloride, and in the case of iridium it is still more so. Iridic chloride, $IrCl_4$, acts as an oxidising agent, readily parts with a fourth of its chlorine to a number of substances, readily evolves chlorine when heated, and it is only at low temperatures that chlorine and aqua regia convert iridium into iridic chloride. In disengaging chlorine iridium more often and easily gives the very stable iridious chloride, $IrCl_3$ (perhaps this substance is Ir_2Cl_6 = $IrCl_2$,$IrCl_4$, insoluble in water, but soluble in potassium chloride, because it forms the double salt K_3IrCl_6), than the dichloride, $IrCl_2$. This compound, corresponding to IrX_3, is very stable, and corresponds with the *basic oxide*, Ir_2O_3, resembling the oxides Fe_2O_3, Co_2O_3. Hence to this form there correspond ammoniacal compounds similar to those given by cobaltic oxide. Although iridium also gives an acid in the form of the salt $K_2Ir_2O_7$, it does not, like iron (and chromium), form the corresponding chloride, $IrCl_6$. In general, in this as in the other elements, it is impossible to judge the chlorine compounds from those with oxygen. Just as there is no chloride SCl_6, but only SCl_2, so also, although $IrO_2(RO)_2$ does exist, still $IrCl_6$ is wanting, and it only gives $IrCl_4$, and this is unstable, like SCl_2, and easily parts with its chlorine. In this respect rhodium is very much like iridium (as platinum is like palladium). It does not seem to form the chloride $RhCl_4$ at all (it probably decomposes with extreme ease) whilst rhodium chloride, $RhCl_3$, is very stable, like many of the salts of the type RhX_3, although after the manner of the platinum elements these salts are easily reduced to metal by the action of heat and powerful reagents. There is as close a resemblance between osmium and ruthenium. Osmium when submitted to the action of dry chlorine gives osmic chloride, $OsCl_4$, but the latter is converted by water (as is osmium by moist chlorine) into osmic anhydride, although the greater portion is then decomposed into $Os(HO)_4$ and 4HCl, like a chloranhydride of an acid. In general this acid character is more developed in osmium than in platinum and iridium. Having parted with chlorine, osmic chloride, $OsCl_4$, gives the un-

$RO_2(HO)_2$ (the type of sulphuric acid); but they, like ferric and manganic acids, are only known in the form of salts of the composition K_2RO_4 or $K_2R_2O_7$ (like the dichromate). These salts are obtained, like the manganates and ferrates, by fusing the oxides, or even the metals themselves, with nitre, or, better still, with potassium peroxide. They are soluble in water, are easily deoxidised, and do not yield the acid anhydrides under the action of acids, but break up, either (like the ferrate) forming oxygen and a basic oxide (iridium and rhodium react in this manner, as they do not give higher forms of oxidation), or passing into a lower and higher form of oxidation—that is, reacting like a manganate (or partly like nitrite or phosphite). Osmium and ruthenium react according to the latter form, as they are capable of giving *higher forms of oxidation* OsO_4 and RuO_4, and therefore their reactions of decomposition may be essentially represented by the equation: $2OsO_3 = OsO_2 + OsO_4$.

Platinum and its analogues, like iron and its analogues, are able to form complex and comparatively stable cyanogen and ammonia compounds, corresponding with the ferrocyanides and the ammoniacal compounds of cobalt, which we have already considered in the preceding chapter.

If platinous chloride, $PtCl_2$ (insoluble in water), is added by degrees to a solution of potassium cyanide, it is completely dissolved (like silver chloride), and on evaporation the solution deposits rhombic prisms of *potassium platinocyanide*, $PtK_2(CN)_4,3H_2O$. This salt, like all those corresponding with it, has a remarkable play of colours, due to the phenomena of dichromism, and even polychromism, natural to all the platinocyanides. Thus it is yellow, and reflects a bright blue light. It is easily soluble in water, effloresces in air, then turns red, and at 100° orange, when it loses all its water. The loss of water does not destroy its stability—that is, it still remains unchanged, and its stability is further shown by the fact that it is formed when potassium ferrocyanide, $K_4Fe(CN)_6$, is heated with platinum black. This salt, first obtained by Gmelin, shows a neutral reaction with litmus; it is exceedingly stable under the action of air, like potassium ferrocyanide, which it resembles in many respects. Thus the platinum in it cannot be discovered by reagents such as sulphuretted hydrogen; the potassium may be replaced by other metals by the action of their salts, so that it corresponds with a whole series of compounds $R_2Pt(CN)_4$,

stable trichloride, $OsCl_3$, and the stable soluble dichloride, $OsCl_2$, which corresponds with platinous chloride in its properties and reactions. The relation of ruthenium to the halogens is of the same nature. These are the most important facts regarding the forms of combination of the platinum metals.

and it is stable, although the potassium cyanide and platinous salt, of which it is composed, individually easily undergo change. When treated with oxidising agents it, like the ferrocyanide, passes into a higher form of combination of platinum. If salts of silver be added to its solution, it gives a heavy white precipitate of silver platinocyanide, $PtAg_2(CN)_4$, which, when suspended in water and treated with sulphuretted hydrogen, enters into double decomposition with the latter and forms insoluble silver sulphide, Ag_2S, and soluble *hydroplatinocyanic acid*, $H_2Pt(CN)_4$. If potassium platinocyanide is mixed with an equivalent quantity of sulphuric acid, then the hydroplatinocyanic acid liberated may be extracted by a mixture of alcohol and ether. The ethereal solution, when evaporated in a desiccator, deposits bright red crystals of the composition $PtH_2(CN)_4,5H_2O$. This acid colours litmus paper, liberates carbonic anhydride from sodium carbonate, and saturates alkalis, so that it presents an analogy to hydroferrocyanic acid.[11]

[11] This acid character is explained by the influence of the platinum on the hydrogen, and by the attachment of the cyanogen groups. Thus cyanuric acid, $H_3(CN)_3O_3$, is an energetic acid compared with cyanic acid, HCNO. And the formation of a compound with five molecules of water of crystallisation confirms the opinion that platinum is able to form compounds of still higher types than that expressed in its saline compounds, and, moreover, the combination of hydroplatinocyanic acid with water does not reach the limit of the compounds which appears in $PtCl_4,2HCl,6H_2O$.

A whole series of *platinocyanides* of the common type $PtR_2(CN)_4nH_2O$ are obtained by means of double decompositions with the potassium or hydrogen or silver salts. For example, the salts of sodium and lithium contain, like the potassium salt, three molecules of water. The sodium salt is soluble in water and alcohol. The ammonium salt has the composition $Pt(NH_4)_2(CN)_4,2H_2O$, and gives crystals which reflect blue and rose-coloured light. This ammonium salt decomposes at 300°, with evolution of water and ammonium cyanide, leaving a greenish *platinum dicyanide*, $Pt(CN)_2$, which is insoluble in water and acid but dissolves in potassium cyanide, hydrocyanic acid, and other cyanides. The same platinous cyanide is obtained by the action of sulphuric acid on the potassium salts in the form of a reddish-brown amorphous precipitate. The most characteristic of the platinocyanides are those of the alkaline earths. The magnesium salt $PtMg(CN)_4,7H_2O$ crystallises in regular prisms, whose side faces are of a metallic green colour and terminal planes dark blue. It shows a carmine-red colour along the main axis, and dark red along the lateral axes; it easily loses water, $2H_2O$, at 40°, and then turns blue (it then contains $5H_2O$, which is frequently the case with the platinocyanides). Its aqueous solution is colourless, and an alcoholic solution deposits yellow crystals. The remainder of the water is given off at 230°. It is obtained by saturating platinocyanic acid with magnesia, and by double decomposition between the barium salt and magnesium sulphate. The strontium salt $SrPt(CN)_4,4H_2O$ crystallises in milk-white plates having a violet and green play of colours. When it effloresces in a desiccator, its surfaces have a violet and metallic green play of colours. A colourless solution of the barium salt $PtBa(CN)_4,4H_2O$ is obtained by saturating a solution of hydroplatinocyanic acid with baryta, or by boiling the insoluble copper platinocyanide in baryta water. It crystallises in monoclinic prisms of a yellow colour, with blue and green reflections; it loses half its water at 100°, and the whole at 150°. Ethyl also gives a very characteristic salt, $Pt(C_2H_5)_2(CN)_4,2H_2O$, whose crystals are isomorphous with those of the potassium salt,

As ammonia, like potassium cyanide, is capable of further combination, so the combination of a platinum salt PtX_2 with ammonia gives

and are obtained by passing hydrochloric acid into an alcoholic solution of hydroplatinocyanic acid.

By the action of chlorine on dilute nitric acid, the platinocyanides are converted into salts of the composition $PtM_2(CN)_5$, which corresponds with $Pt(CN)_3,2KCN$—that is, they express the type of a non-existent form of oxidation of platinum, PtX_3 (*i.e.* oxide Pt_2O_3), just as potassium ferricyanide ($FeCy_3KCy$) corresponds with ferric oxide, and the ferrocyanide corresponds with the ferrous oxide. The potassium salt of this series contains $PtK_2(CN)_5,3H_2O$, and forms brown regular prisms with a metallic lustre, and is soluble in water but insoluble in alcohol. Alkalis re-convert this compound into the ordinary platinocyanide $K_2Pt(CN)_4$, taking up the excess of cyanogen. It is remarkable that the salts of the type PtM_2Cy_5 contain the same amount of water of crystallisation as those of the type PtM_2Cy_4. Thus the salts of potassium and lithium contain three, and the salt of magnesium seven, molecules of water, like the corresponding salts of the type of platinous oxide. Moreover, neither platinum nor any of its associates gives any cyanogen compound corresponding with the oxide, *i.e.* having the composition PtK_2Cy_6, just as there are no compounds higher than those which correspond to $RCy_3,nMCy$ for cobalt or iron. This would appear to indicate the absence of any such cyanides, and indeed, for no element are there yet known any poly-cyanides containing more than three equivalents of cyanogen for one equivalent of the element. This phenomenon is perhaps connected with the faculty of cyanogen to give tricyanogen polymerides, such as cyanuric acid, solid cyanogen chloride, &c. It is also necessary to turn attention to the fact that ruthenium and osmium—which, as we know, give higher forms of oxidation than platinum—are also able to combine with a larger proportion of potassium cyanide (but not of cyanogen) than platinum. Thus ruthenium forms a crystalline *hydroruthenocyanic acid*, $RuH_4(CN)_6$, which is soluble in water and alcohol, and corresponds with the salts $M_4Ru(CN)_6$. There are exactly similar osmic compounds—for example, $K_4Os(CN)_6,3H_2O$. The latter is obtained in the form of colourless, sparingly-soluble regular tablets on evaporating the solution obtained from a fused mixture of potassium osmiochloride, K_2OsCl_6, and potassium cyanide. These osmic and ruthenic compounds fully correspond with potassium ferrocyanide, $K_4Fe(CN)_6,3H_2O$, not only in their composition but also in their crystalline form and reactions, which again demonstrates the close analogy between iron, ruthenium, and osmium, which we have shown by giving these three elements a similar position (in the eighth group) in the periodic system. For rhodium and iridium there are known only salts of the same type as the ferricyanides, M_3RCy_6, and for palladium only of the type M_2PdCy_4, which are analogous to the platinum salts. In all this one cannot but see a *constancy of the types* of the double cyanides. In the eighth group we have iron, cobalt, nickel, copper, and their analogues ruthenium, rhodium, palladium, silver, and also osmium, iridium, platinum, gold. The double cyanides of iron, ruthenium, osmium have the type $K_4R(CN)_6$; of cobalt, rhodium, iridium, the type $K_3R(CN)_6$; of nickel, palladium, platinum the type $K_2R(CN)_4$ and $K_2R(CN)_5$; and for copper, silver, gold there are known $KR(CN)_2$, so that the presence of 4, 3, 2, and 1 atoms of potassium (in the higher proportion) corresponds with the order of the elements in the periodic system. Those types which we have seen in the ferrocyanides and ferricyanides of iron repeat themselves in all the platinoid metals, and this involuntarily leads one to conclude that the formation of similar so-called double salts is of exactly the same nature as that of the ordinary salts. If, for the expression of the bond of the elements in the oxygen salts, one recognises the existence of an *aqueous residue* (hydroxyl group), in which the hydrogen is replaced by a metal; then we have only to apply this mode of expression to the double salts and the analogy will be obvious, if we only remember that Cl_2, $(CN)_2$, SO_4, &c., are equivalent to O, as we see in RO, RCl_2, RSO_4, &c. Therefore, wherever OH can be placed, there we can also place Cl_2H, $(CN)_2H$, SO_4H, &c. Thus the double salt $MgSO_4,K_2SO_4$, according to this reasoning, *may be* counted as a substance of the same

just such stable compounds as are obtained by means of the cyanogen compounds. But as ammonia does not contain any hydrogen easily

type as $MgCl_2$, namely, $=Mg(SO_4K)_2$, and the alums as containing $Al(OH)(SO_4)$, namely, as $Al(SO_4K)(SO_4)$. It is also possible to take the water of crystallisation into account here. It may also be introduced into such formulæ as the above, but we will not linger over this digression and only apply these considerations to the type of the ferrocyanides and ferricyanides and their platinum analogues. Such a salt as K_2PtCy_4 therefore may be regarded as $Pt(Cy_2K)_2$, like $Pt(OH)_2$; and such a salt as PtK_2Cy_5 as $PtCy(Cy_2K)_2$, the analogue of $PtX(OH)_2$, or $AlX(OH)_2$, and other compounds of the type RX_3. Potassium ferricyanide and the analogous compounds of cobalt, iridium, and rhodium, belong to the same type, with the same difference as there is between $RX(OH)_2$ and $R(OH)_3$, because $FeK_3Cy_6 = Fe(Cy_2K)_3$. Limiting myself to these considerations, which may partially elucidate the nature of double salts, I will now pass again to the complex saline compounds known for platinum.

On mixing a solution of potassium thiocyanate with a solution of potassium platinosochloride, K_2PtCl_4, they form a double thiocyanate, $PtK_2(CNS)_4$, which is easily soluble in water and alcohol, crystallises in red prisms, and gives an orange-coloured solution, which precipitates salts of the heavy metals. The action of sulphuric acid on the lead salt of the same type gives the acid itself, $PtH_2(SCN)_4$, which corresponds with these salts. The type of these compounds is evidently the same as that of the cyanides.

Platinous chloride, $PtCl_2$, which is insoluble in water, forms *double salts with the metallic chlorides*. These double chlorides are soluble in water, and capable of crystallising. Hence when a hydrochloric acid solution of platinous chloride is mixed with solutions of metallic salts and evaporated it forms crystalline salts of a red or yellow colour. Thus, for example, the potassium salt, PtK_2Cl_4, is red, and easily soluble in water; the sodium salt is also soluble in alcohol; the barium salt, $PtBaCl_4,3H_2O$, is soluble in water, but the silver salt, $PtAg_2Cl_4$, is insoluble in water, and may be used for obtaining the remaining salts by means of double decomposition with their chlorides.

A remarkable example of the complex compounds of platinum was observed by Schützenberger. He showed that finely-divided platinum in the presence of chlorine and carbonic oxide at 300° gives phosgene and a volatile compound containing platinum. A similar substance is formed by the action of carbonic oxide on platinous chloride. It is decomposed with explosion by water. Carbon tetrachloride dissolves a portion of this substance, and on evaporation gives crystals of $2PtCl_2,3CO$, whilst the compound $PtCl_2,2CO$ remains undissolved. When fused and sublimed it gives yellow needles of $PtCl_2,CO$, and in the presence of an excess of carbonic oxide $PtCl_2,2CO$ is formed. These compounds are fusible (the first at 250°, the second at 142°, and the third at 195°). In this case (as in the double cyanides) combination takes place, because both carbonic oxide and platinous chloride are unsaturated compounds capable of further combination.

The faculty of platinous chloride for forming particularly stable compounds with divers substances which on their side have the faculty for further combination (like potassium cyanide or carbonic oxide), shows itself in the formation of the compound $PtCl_2,PCl_3$ by the action of phosphorus pentachloride at 250° on platinum powder. The product contains both phosphorus pentachloride and platinum, whilst the presence of $PtCl_2$ is shown from the fact that the action of water produces *chlorplatino-phosphorous acid*, $PtCl_2P(OH)_3$. It evidently corresponds, on the one hand, with phosphoric acid, and, on the other hand, with those products which are formed by the complication of $PtCl_2$.

After the cyanides, the *double salts* of platinum *formed by sulphurous acid* are most distinguished for their stability and characteristic properties. This is all the more instructive as sulphurous acid is only feebly energetic, and moreover in these, as in all its compounds, it exhibits a dual reaction. The salts of sulphurous acid, R_2SO_3, either react as salts of a feeble bibasic acid, where the group SO_3 presents itself as bivalent, and consequently equal to X_2, or else they react after the manner of salts of a monobasic

replaceable by metals, and as ammonia itself is able to combine with acids, so the PtX_2 plays, as it were, the part of an acid with reference

acid containing the same residue, RSO_3, as occurs in the salts of sulphuric acid. In sulphurous acid this residue is combined with hydrogen, $H(SO_3H)$, whilst in sulphuric acid it is united with the aqueous residue (hydroxyl), $OH(SO_3H)$. These two forms of action of the sulphites appear in their reactions with the platinum salts—that is to say, salts of both kinds are formed, and they both correspond with the type PtH_2X_4. The one series of salts contain $PtH_2(SO_3)_2$, and their reactions are due to the bivalent residue of sulphurous acid, which replaces X_2. The others, which have the composition $PtR_2(SO_3H)_4$, contain sulphoxyl. Therefore the latter salts will evidently react like acids, and if we did not differentiate the hydrogen here contained they would be represented as $PtR_2H_2(SO_3)_4$. But then we might suppose that these salts were formed from other sources, which is not true, because the salts of this kind are formed simultaneously with the salts of the first kind, and pass into them. These salts are obtained either by directly dissolving platinous oxide in water containing sulphurous acid, or by passing sulphurous anhydride into a solution of platinous chloride in hydrochloric acid. It may therefore be supposed that these salts contain platinous sulphite, $PtSO_3$, but it is unknown in a free state, and only appears in the form of double salts. Thus, if a solution of platinous chloride or platinous oxide in sulphurous acid be saturated with sodium carbonate, it forms a white, sparingly soluble precipitate containing $PtNa_2(SO_3Na)_4,7H_2O$. If this precipitate is dissolved in a small quantity of hydrochloric acid and left to evaporate at the ordinary temperature, it deposits a salt of the other type, $PtNa_2(SO_3)_2,H_2O$, in the form of a yellow powder, which is sparingly soluble in water. The potassium salt analogous to the first salt, $PtK_2(SO_3K)_4,2H_2O$, is precipitated by passing sulphurous anhydride into a solution of potassium sulphite in which platinous oxide is suspended. A similar salt is known for ammonium, and with hydrochloric acid it gives a salt of the second kind, $Pt(NH_4)_2(SO_3)_2,H_2O$. If ammonio-chloride of platinum be added to an aqueous solution of sulphurous anhydride, it is first deoxidised, and chlorine is evolved, forming a salt of the type PtX_2; a double decomposition then takes place with the ammonium sulphite, and a salt of the composition $Pt(NH_4)_2Cl_3(SO_3H)$ is formed (in a desiccator). The acid character of this substance is explained by the fact that it contains the elements SO_3H—sulphoxyl, with the hydrogen not yet displaced by a metal. On saturating a solution of this acid with potassium carbonate it gives orange-coloured crystals of a potassium salt of the composition $Pt(NH_4)_2Cl_3(SO_3K)$. Here it is evident that an equivalent of chlorine in $Pt(NH_4)_2Cl_4$ is replaced by the univalent residue of sulphurous acid. Among these salts, that of the composition $Pt(NH_4)_2Cl_2(SO_3H)_2,H_2O$ is very readily formed, and crystallises in well-formed colourless crystals; it is obtained by dissolving ammonium platinosochloride, $Pt(NH_4)_2Cl_4$, in an aqueous solution of sulphurous acid. The difficulty with which sulphurous anhydride and platinum are separated from these salts indicates the same basic character in these compounds as is seen in the double cyanides of platinum. In their passage into a complex salt, the metal platinum and the group SO_2 modify their relations (compared with those of PtX_2 or SO_2X_2), just as the chlorine in the salts KClO, $KClO_3$, and $KClO_4$ is modified in its relations as compared with hydrochloric acid or potassium chloride.

No less characteristic are the *platinonitrites* formed by platinous oxide. They correspond with nitrous acid, whose salts, RNO_2, contain the univalent radicle NO_2, which is capable of replacing chlorine, and therefore the salts of this kind should form a common type $PtR_2(NO_2)_4$, and such a salt of potassium has actually been obtained by mixing a solution of potassium platinosochloride with a solution of potassium nitrite, when the liquid becomes colourless, especially if it be heated, which indicates the change in the chemical distribution of the elements. As the liquid decolorises it gradually deposits sparingly soluble, colourless prisms of the potassium salt $K_2Pt(NO_2)_4$, which does not contain any water. With silver nitrate a solution of this salt gives a precipitate of silver platinonitrite, $PtAg_2(NO_2)_4$. The silver of this salt may be replaced by other

to the ammonia. Owing to the influence of the ammonia, the X_2 in the resultant compound will present the same character as it has in ammoniacal salts; consequently, the ammoniacal compounds produced from PtX_2 will be salts in which X will be replaceable by various other haloids, just as the metal is replaced in the cyanogen salts, such is the nature of the *platino-ammonium compounds*. PtX_2 forms compounds with $2NH_3$ and with $4NH_3$, and so also PtX_4 gives (but not directly from PtX_4 and ammonia, but from the compounds of PtX_2 by the action of chlorine, &c.) like compounds with $2NH_3$ and with $4NH_3$.[12]

metals by means of double decomposition with metallic chlorides. The sparingly soluble barium salt, when treated with an equivalent quantity of sulphuric acid, gives a soluble acid, which separates, under the receiver of an air-pump, in red crystals; this is probably an acid of the composition $PtH_2(NO_2)_4$.

[12] The platinum salt and ammonia, when once combined together, are no longer subject to their ordinary reactions, but form comparatively very stable compounds. The self-evident question occurs to all who are acquainted with these phenomena, as to what is the relation of the elements contained in these compounds. The first explanation which suggests itself is that these compounds are salts of ammonium in which the hydrogen is partially replaced by platinum. This is the view, with certain shades of difference, held by many respecting the platino-ammonium compounds. They were regarded in this light by Gerhardt, Schiff, Kolbe, Weltzien, and many others. If we suppose the hydrogen in $2NH_4X$ to be replaced by bivalent platinum (as in the salts PtX_2), then we shall obtain $\begin{matrix}NH_3\\NH_3\end{matrix}Pt\begin{matrix}X\\X\end{matrix}$—that is, the compound $PtX_2,2NH_3$. The compound with $4NH_3$ will then be represented by a further substitution of the hydrogen in ammonia by ammonium itself—*i.e.* as $NH_2(NH_4X)_2Pt$—that is, we shall obtain the compound $PtX_2,4NH_3$. A modification of this view is found in that representation of compounds of this kind which is based on atomicity. As platinum in PtX_2 is bivalent, has two affinities, and ammonia, NH_3, is also bivalent, because nitrogen is quinquivalent and is here only combined with H_3, it is evident what bonds should be represented in $PtX_2 2NH_3$ and in $PtX_2 4NH_3$. In the former $Pt(NH_3Cl)_2$ the nitrogen of each atom of ammonia is united by three affinities with H_3, by one with platinum, and by the fifth with chlorine. The other compound is $Pt(NH_3{\cdot}NH_3Cl)_2$—that is, the N is united by one affinity with the other N, whilst the remaining bonds are the same as in the first salt. It is evident that this union or chain of ammonias has no obvious limit, and the most essential fault of such a mode of representation is that it does not indicate at all what number of ammonias are capable of being retained by platinum. Moreover, it is hardly possible to admit the bond between nitrogen and platinum in such stable compounds, for these kinds of affinities are, at all events, feeble and cannot lead to stability, but would rather indicate explosive and easily-decomposed compounds. Moreover, it is not clear why this platinum, which is capable of giving PtX_4, does not act with its remaining affinities when the addition of ammonia to PtX_2 takes place. These and certain other considerations which indicate the imperfection of this representation of the structure of the platino-ammonium salts, cause many chemists to incline more to the representations of Berzelius, Claus, Gibbs, and others, who suppose that NH_3 is able to combine with substances, to adjoin itself or pair itself with them (this kind of combination is called 'Paarung') without altering the fundamental capacity of a substance for further combinations. Thus, in $PtX_2,2NH_3$, the ammonia is the associate of PtX_2, which is expressed by the formula $N_2H_6-PtX_2$. Without enlarging on the exposition of the details of this doctrine, we will only mention that it, like the first, does not render it possible to foresee a limit to the compounds with ammonia; it isolates compounds of this kind

If ammonia acts on a boiling solution of platinous chloride in hydrochloric acid, it produces the green *salt of Magnus* (1829),

into a special and artificial class; does not show the connection between compounds of this and of other kinds, and therefore it essentially only expresses the fact of the combination with ammonia and the modification in its ordinary reactions. Hence for these reasons we do not hold to either of these proposed representations of the ammonio-platinum compounds, but regard them from the point of view cited above with reference to double salts and water of crystallisation—that is, we embrace all these compounds under the representation of complex compounds higher than saline compounds. The type of the compound $PtX_2,2NH_3$ is far more probably the same as that of $PtX_2 2Z$—*i.e.* as PtX_4, or, still more accurately and truly, it is a compound of the same type as $PtX_2,2KX$ or $PtX_2,2H_2O$, &c. In PtK_2X_4, although the platinum has entered into the type PtX_2, yet its character has changed in the same manner as the character of sulphur changes when from SO_2 the compound $SO_2(OH)_2$ is obtained, or when $KClO_4$ is obtained from KCl. For us as yet there is no question as to *what* affinities hold X_2 and what hold $2NH_3$, because this is a question which arises from the supposition of the existence of different affinities in the atoms, which there is no reason for taking as a common phenomenon. It seems to us that it is most important *as a commencement* to render clear the analogy in the formation of various complex compounds, and it is this analogy of the ammonia compounds with those of water of crystallisation and double salts that forms the main object of the primary generalisation. We recognise in platinum, at all events, not only the four affinities expressed in the compound $PtCl_4$, but a much larger number of them, if only the *summation of affinities* is actually possible. Thus, in sulphur we recognise not two but a much greater number of affinities; it is clear that at least six affinities can act. So also among the analogues of platinum: osmic anhydride, OsO_4, indicates the existence of at least eight affinities; whilst, in chlorine, judging from the compound $KClO_4 = ClO_5(OK) = ClX_7$, we must recognise at least seven affinities, instead of the one which is accepted. The latter mode of calculating affinities is a tribute to that period of the development of science when only the simplest hydrogen compounds were considered, and when all complex compounds were entirely neglected (they were placed under the class of molecular compounds). This is insufficient for the present store of data, because we find that, in complex compounds as in the most simple, the same constant types or cases of equilibrium are repeated, and the character of certain elements is deeply modified in the passage from the most simple into very complex compounds.

Judging from the most complex platino-ammonium compounds $PtCl_4,4NH_3$, one should admit the possibility of the formation of compounds of the type PtX_1Y_4, where $Y_4 = 4X_2 = 4NH_3$, and this shows that those forces which form such a characteristic series of double platinocyanides $PtM_2(CN)_4,3H_2O$, probably also determine the formation of the higher ammonia derivatives, as is seen on comparing—

$PtCl_2$	NH_3	Cl_2	$3NH_3$
$Pt(CN)_2$	KCN	KCN	$3H_2O$.

Moreover, it is obviously much more natural to ascribe the faculty for combination with nY to the whole of the acting elements—that is, to PtX_2 or PtX_4, and not to platinum alone. Naturally such compounds are not produced with any Y. With certain X's there only combine certain Y's. The best known and most frequently-formed compounds of this kind are those with water—that is, compounds with water of crystallisation. Besides these, we know of compounds with salts; these are double salts; also we know that similar compounds are also frequently formed by means of ammonia. Salts of zinc, ZnX_2, copper, CuX_2, silver, AgX, and many others give like compounds, but these and many other *ammonio-metallic* saline compounds are unstable, and readily part with their combined ammonia, and it is only in the elements of the platinum group, and in the group of the analogues of iron, that we observe the faculty to form stable ammonio-metallic compounds. One cannot but turn attention to

$PtCl_2,2NH_3$, insoluble in water and hydrochloric acid. But, judging by its reactions, this salt is twice as complex. Thus, Gros (1837), on boiling Magnus's salt with nitric acid, observed that half the chlorine was replaced by the residue of nitric acid and half the platinum was disengaged: $2PtCl_2(NH_3)_2+2HNO_3=PtCl_2(NO_3)_2(NH_3)_4+2PtCl_2$. The Gros's salt thus obtained is soluble in water, and the elements of nitric acid, but not the chlorine, contained in it are capable of easily submitting themselves to double saline decomposition. Thus silver nitrate does not enter into double decomposition with the chlorine of Gros's salt. Most instructive was the circumstance that Gros, by acting on his salt with hydrochloric acid, succeeded in substituting the residue of nitric acid in it by chlorine, and thus introduced chlorine, which easily reacted with silver nitrate. Thus it appeared that Gros's salt contained two varieties of chlorine—one which reacts readily, and the other which reacts with difficulty. The composition of Gros's first salt is $PtCl_2(NH_3)_4(NO_3)_2$; it may be converted into $PtCl_2(NH_3)_4(SO_4)$, and in general into $PtCl_2(NH_3)_4X_2$.[13]

the fact that the metals of the platinum and iron groups are able to form several high grades of oxidation which have an acid character, and consequently in the lower degrees of combination there yet remain affinities capable of retaining other elements, and they probably retain ammonia, and hold it the more stably, because all the properties of the platinum compounds are rather acid than basic—that is, PtX_n recalls rather HX or SnX_n or CX_n than KX, CaX_2, BaX_2, &c., and ammonia naturally will rather combine with an acid than with a basic substance. Further, a dependence, or certain connection of the forms of oxidation with the ammonia compounds, is seen on comparing the following compounds:

$PdCl_2,2NH_3,H_2O$	$PdCl_2,4NH_3,H_2O$
$PtCl_2,2NH_3$	$PtCl_4,4NH_3$
$RhCl_3,5NH_3$	$RuCl_2,4NH_3,3H_2O$
$IrCl_3,5NH_3$	$OsCl_2,4NH_3,2H_2O$

We know that platinum and palladium give compounds of lower types than iridium and rhodium, whilst ruthenium and osmium give the highest forms of oxidation; this shows itself in this case also. We have purposely cited the same compounds with $4NH_3$ for osmium and ruthenium as we have for platinum and palladium, and it is then seen that Ru and Os are capable of retaining $2H_2O$ and $3H_2O$, besides Cl_2 and NH_3, which the compounds of platinum and palladium are unable to do.

All the platinum metals give very stable *metallo-ammonium compounds*, undecomposable by water, dilute acids, and alkalis, like the compounds of platinum, which we describe in fuller detail, such as the salts of Reiset's second base, $PtX_2,2NH_3$, the salts of Reiset's first base, $PtX_2,4NH_3$, Gerhardt's salts, $PtX_4,2NH_3$, and Gros's salts, $PtX_4,4NH_3$.

Similar salts have been already obtained for palladium and iridium (Skoblikoff), and the two first kinds for osmium and ruthenium also. Iridium and rhodium, which easily give compounds of the type RX_3, give compounds (Claus) of the type $IrX_3,5NH_3$, of a rose colour, and $RhX_3,5NH_3$, of a yellow colour. Jörgensen, in his researches on these compounds, showed their entire analogy with the cobalt compounds, as was to be expected from the periodic system.

[13] Subsequently, a whole series of such compounds was obtained with various elements in the place of the (non-reacting) chlorine, and nevertheless they, like the

The salt of Magnus when boiled with a solution of ammonia gives the salt (of Reiset's first base) $PtCl_2(NH_3)_4$, and this, when treated with bromine, forms the salt $PtCl_2Br_2(NH_3)_4$, which is composed and reacts like Gros's salt. To Reiset's salts there corresponds a soluble, colourless, crystalline *hydroxide*, $Pt(OH)_2(NH_3)_4$. It is a powerful and perfectly energetic *alkali*; it attracts carbonic anhydride from the atmosphere, precipitates metallic salts like potash, saturates active acids, even sulphuric, forming colourless (with nitric, carbonic, and hydrochloric acids), or yellow (with sulphuric acid), salts of the type $PtX_2(NH_3)_4$.[14]

chlorine, reacted with difficulty, whilst the second portion of the X's introduced into such salts easily underwent reaction. This formed the most important reason for the interest which the study of the composition and structure of the platino-ammonium salts subsequently presented to many chemists, such as Reiset, Blomstrand, Peyrone, Radeffski, Gerhardt, Buckton, Cleve, Thomsen, and others. The salts $PtX_4,2NH_3$, discovered by Gerhardt, also exhibited several different properties in the two pairs of X's. In the remaining platino-ammonium salts all the X's appear to react alike.

The quality of the X's, retainable in the platino-ammonium salts, may be considerably modified, and they may frequently be wholly or partially replaced by hydroxyl. For example, the action of ammonia on the nitrate of Gerhardt's base, $Pt(NO_3)_4,2NH_3$, in a boiling solution gradually produces a yellow crystalline precipitate, which is nothing else than a hydroxide, $Pt(OH)_4 2NH_3$. It is sparingly soluble in water, but immediately gives soluble salts $PtX_4,2NH_3$ with acids. The stability of this hydroxide is such that potash does not expel ammonia from it, even on boiling, and it does not change below 180°. Similar properties are shown by the hydroxide $Pt(OH)_2,2NH_3$ and the oxide $PtO,2NH_3$ of Reiset's second base. But the hydroxides of the compounds containing $4NH_3$ are particularly remarkable. The presence of ammonia renders them soluble and energetic.

[14] Hydroxides are known corresponding with Gros's salts, which contain one hydroxyl group in the place of that chlorine or haloid which in Gros's salts reacts with difficulty, and these hydroxides do not show the direct properties of alkalis, just as the chlorine which stands in the same place does not react distinctly; but still, after the prolonged action of acids, this hydroxyl group is also replaced by acids. So, for example, the action of nitric acid on $Pt(NO_3)_2Cl_2,4NH_3$ causes the non-active chlorine to react, but in the result all the chlorine is not replaced by NO_3, but only half, and the other half is replaced by the hydroxyl group: $Pt(NO_3)_2Cl_2,4NH_3 + HNO_3 + H_2O = Pt(NO_3)_3(OH),4NH_3 + 2HCl$; and this is particularly characteristic, because here the hydroxyl group has not reacted with the acid—an evident sign of the non-alkaline character of the residue in this case.

To the common properties of the platino-ammonium salts, we must add not only their *stability* (feeble acids and alkalis do not decompose them, the ammonia is not evolved by heating, &c.), but also the fact that the ordinary reactions of platinum are concealed in them to as great an extent as those of iron in the ferricyanides. Thus neither alkalis nor hydrogen sulphide will separate the platinum from them. For example, sulphuretted hydrogen in acting on Gros's salts gives sulphur, removes half the chlorine by means of its hydrogen, and forms salts of Reiset's first base. This may be understood or explained to oneself by counting the platinum in the molecule as covered, walled up by the ammonia, and situated in the centre of the molecule, and therefore inaccessible to reagents. But then one would expect to find clearly-expressed ammoniacal properties, and this is not the case. Thus ammonia is easily decomposed by chlorine, whilst in acting on the platino-ammonium salts containing PtX_2 and $2NH_3$ or $4NH_3$, chlorine combines and does not destroy the ammonia; it converts Reiset's salts into those of Gros and Gerhardt. Thus from $PtX_2,2NH_3$ there proceeds $PtX_2Cl_2,2NH_3$, and from $PtX_2,4NH_3$ there proceeds salt of Gros's base $PtX_2Cl_2,4NH_3$. This shows that the amount of chlorine which com-

The stability of such compounds, and the existence of many other compounds analogous to them, endows them with a particular chemical

bines is not dependent on the amount of ammonia present, but only conforms itself with the basic property of platinum. Owing to this some chemists suppose the ammonia to be inactive or passive in certain compounds. It appears to me that these relations, these modifications, in the usual properties of ammonia and platinum are explained directly by their mutual combination. Sulphur, in sulphurous anhydride, SO_2, and hydrogen sulphide, SH_2, is naturally one and the same, but if we only knew of it in the form of hydrogen sulphide, then, having obtained it in the form of sulphurous anhydride, we should consider its properties as hidden. The oxygen in magnesia, MgO, and in nitric peroxide, NO_2, is so different that there is no resemblance. Arsenic no longer reacts in its compounds with hydrogen as it reacts in its compounds with chlorine, and in their compounds with nitrogen all metals modify both their reactions and their physical properties. We are accustomed to judge the metals by their saline compounds with haloid groups, and ammonia by its compounds with acid substances, and here, in the platino-compounds, if we assume the platinum to be bound to the entire mass of the ammonia—to its hydrogen and nitrogen—we shall understand that both the platinum and ammonia modify their characters. Far more complicated is the question why a portion of the chlorine (and other haloid simple and complex groups) in Gros's salts acts in a different manner from the other portion, and why only half of it acts in the usual way. But this also is not an exclusive case. The chlorine in potassium chlorate or in carbon chloride does not react with the same ease with metals as the chlorine in the salts corresponding with hydrochloric acid. There it is united to oxygen and carbon, here it is united partly to platinum and partly to the platino-ammonium group. Many chemists, moreover, suppose that a part of the chlorine is united directly to the platinum and the other part to the nitrogen of the ammonia, and thus explain the difference of the reactions; but chlorine united to platinum reacts as well with a silver salt as the chlorine of ammonium chloride, NH_4Cl, or nitrosyl chloride, NOCl, although no one denies that here there is a union between the chlorine and nitrogen. Hence it is necessary to explain the absence of a facile reactive capacity in a portion of the chlorine by the conjoint influence of the platinum and ammonia on it, whilst the other portion may be admitted as being under the influence of the platinum only, and therefore as reacting as in other salts. By admitting a certain kind of stable union in the platino-ammonium grouping it is possible to imagine that the chlorine does not react with its customary facility, because access to a portion of the atoms of chlorine in this complex grouping is difficult and the chlorine union is not the same as we usually meet in the saline compounds of chlorine. These are the bases on which we, in refuting the now accepted explanations of the reactions and formation of the platino-compounds, pronounce that opinion as to their structure which follows.

In characterising the platino-ammonium compounds, it is necessary to keep in mind that compounds which already contain PtX_4 do not combine directly with NH_3, and that such compounds as $PtX_4,4NH_3$ only proceed from PtX_2, and therefore it is natural to conclude that those affinities and forces which cause PtX_2 to combine with X_2 also cause it to combine with $2NH_3$. And having the compound $PtX_2,2NH_3$, and supposing that in subsequently combining with Cl_2 it reacts with those affinities which produce the compounds of platinic chloride, $PtCl_4$, with water, potassium chloride, potassium cyanide, hydrochloric acid, and the like, we explain not only the fact of combination, but also many of the reactions occurring in the transition of one kind of platino-ammonium salts into another. Thus by this means we explain the fact that (1) $PtX_2,2NH_3$ combines with $2NH_3$, forming salts of Reiset's first base; (2) and the fact that this compound (represented as follows for distinctness), $PtX_2,2NH_3,2NH_3$, when heated, or even when boiled in solution, again passes into $PtX_2,2NH_3$ (which resembles the easy disengagement of water of crystallisation, &c.); (3) the fact that $PtX_2,2NH_3$ is capable of absorbing, under the action of the same forces, a molecule of chlorine, $PtX_2,2NH_3,Cl_2$, which it

interest. Thus Kurnakoff (1889) obtained a series of corresponding compounds containing thiocarbamide, CSN_2H_4, in the place of ammonia; $PtCl_2,4CSN_2H_4$, and others corresponding with Reiset's salts. Hydroxylamine, and other substances corresponding with ammonia, also give similar compounds.

then retains with energy, because it is attracted, not only by the platinum, but also by the hydrogen of the ammonia; (4) the fact that this chlorine held in this compound (of Gerhardt) will have a position unusual in salts, which will explain a certain (although very feebly-developed) difficulty of reaction; (5) the fact that this does not exhaust the faculty of platinum for further combination (it is enough to remember the compound $PtCl_4,2HCl,16H_2O$), and therefore both $PtX_2,2NH_3,Cl_2$ and $PtX_2,2NH_3,2NH_3$ are still capable of combination, whence the latter, with chlorine, gives $PtX_2,2NH_3,2NH_3,Cl_2$, after the type of PtX_4Y_4 (and perhaps higher); (6) the fact that Gros's compounds thus formed are readily re-converted into the salts of Reiset's first base when acted on by reducing agents; (7) the fact that in Gros's salts, $PtX_2,2NH_3,(NH_3X)_2$, the newly-attached chlorine or haloid will react with difficulty with salts of silver, &c., because it is attached both to the platinum and to the ammonia, for both of which it has an attraction; (8) the fact that the faculty for further combination is not even yet exhausted in the type of Gros's salts, and that we actually have a compound of Gros's chlorine salt with platinous chloride and with platinic chloride; the salt $PtSO_4,2NH_3,2NH_3,SO_4$ combines further also with H_2O; (9) the fact that such a faculty for combination with new molecules is naturally more developed in the lower forms of combination than in the higher. Therefore the salts of Reiset's first base—for example, $PtCl_2,2NH_3,2NH_3$—both combine with water and give precipitates (soluble in water but not in hydrochloric acid) of double salts with many salts of the heavy metals—for example, with lead chloride, cupric chloride, and also with platinic and platinous chlorides (Buckton's salts). The latter compounds will have the composition $PtCl_2,2NH_3,2NH_3,PtCl_2$—that is, the same composition as the salts of Reiset's second base, but it cannot be identical with it. Such an interesting case does actually exist. The first salt, $PtCl_2,4NH_3,PtCl_2$, is green, insoluble in water and in hydrochloric acid, and is known as *Magnus's salt*, and the second, $PtCl_2,2NH_3$, is Reiset's yellow, sparingly soluble (in water). They are polymeric, namely, the first contains twice the number of elements held in the second, and at the same time they easily pass into each other. If ammonia be added to a hot hydrochloric acid solution of platinous chloride, it forms the salt $PtCl_2,4NH_3$, but in the presence of an excess of platinous chloride it gives Magnus's salt. On boiling the latter in ammonia it gives a colourless soluble salt of Reiset's first base, $PtCl_2,4NH_3$, and if this is boiled with water, then ammonia is disengaged, and a salt of Reiset's second base, $PtCl_2,2NH_3$, is obtained.

A class of platino-ammonium isomerides (obtained by Millon and Thomsen) are also known. Buckton's salts—for example, the copper salt—were obtained by them from the salts of Reiset's first base, $PtCl_2,4NH_3$, by treatment with a solution of cupric chloride, &c., and therefore, according to our method of expression, Buckton's copper salt will be $PtCl_2,4NH_3,CuCl_2$. This salt is soluble in water, but not in hydrochloric acid. In it the ammonia must be considered as united to the platinum. But if cupric chloride be dissolved in ammonia, and a solution of platinous chloride in ammonium chloride is added to it, then a violet precipitate is obtained of the same composition as Buckton's salt, but which is insoluble in water but soluble in hydrochloric acid. In this a portion, if not all, of the ammonia must be regarded as united to the copper, and it must therefore be represented as $CuCl_2,4NH_3,PtCl_2$. This form is identical in composition but different in properties (is isomeric) with the preceding salt (Buckton's). The salt of Magnus is intermediate between them, $PtCl_2,4NH_3,PtCl_2$; it is insoluble in water and hydrochloric acid. These and certain other instances of isomeric compounds in the series of the platino-ammonium salts throw a light on the nature of the compounds in question, just as the study of the isomerides of the carbon compounds has served and still serves as the chief cause of the rapid progress of organic chemistry.

CHAPTER XXIV

COPPER, SILVER, AND GOLD

THAT degree of analogy and difference which exists between iron, cobalt, and nickel repeats itself in the corresponding triad ruthenium, rhodium, and palladium, and also in the heavy platinum metals, osmium, iridium, and platinum. These nine metals form the VIII. group of the elements in the periodic system, being the intermediate group between the even elements of the large periods and the uneven, among which we know zinc, cadmium, and mercury in the II. group. Copper, silver, and gold complete[1] this transition, because their properties place them in proximity to nickel, palladium, and platinum on the one hand, and to zinc, cadmium, and mercury on the other. Thus, for example, the atomic weight of copper Cu=63, and in all its properties it stands between Ni=59 and Zn=65. But as the transition from the VIII. group to the II. group, where zinc is situated, cannot be otherwise than through the I. group, so in copper there are certain properties of the elements of the I. group. Thus it gives a sub-oxide, Cu_2O, and salts, CuX, like the elements of the I. group, although at the same time it forms an oxide, CuO, and salts, CuX_2, like nickel and zinc.

In the state of the oxide, CuO, and the salts, CuX_2, copper is analogous to zinc, judging from the solubility, isomorphism, and other characters. So, for instance, cupric sulphate forms isomorphous mixtures with the sulphates of the magnesium group, in which the amount of water of crystallisation varies readily according to the temperature,[2]

[1] The perfectly unique position held by copper, silver, and gold in the periodic system of the elements, and the degree of affinity which is found between them, is all the more remarkable, as nature and practice have long isolated these metals from all others by having employed them—for example, for metallic money—and determined their relative importance and value in conformity with the order (silver between copper and gold) of their atomic weights, &c.

[2] Cupric sulphate contains 5 molecules of water, $CuSO_4,5H_2O$, and the isomorphous mixtures with $ZnSO_4,7H_2O$ contain either 5 or 7 equivalents, according to whether copper or zinc predominates. If there be a large proportion of copper, and if the mixture contains $5H_2O$, then the form of the isomorphous mixture (triclinic) will be isomorphous

and the relative quantities of the metals varies in divers proportions, as is the case in all other isomorphous mixtures of similar metals. The facility of the transition from the cupric salts corresponding with the oxide CuO into the cuprous salts corresponding with the suboxide Cu_2O, and the relative proportion of the metal in both compounds, gives an easy means of accurately determining the relative composition of both of these oxides of copper. Ascribing the formula RO to the oxides of the magnesium group, that of the suboxide of copper, judging by the amount of oxygen it contains, should be R_2O, corresponding with the oxides of the alkali metals. In the cuprous salts there is undoubtedly a great resemblance to the silver salts—thus, for example, silver chloride, AgCl, is characterised by its insolubility and capacity to combine with ammonia. Cuprous chloride closely resembles it, for it is also insoluble in water, and combines with ammonia and dissolves in it, &c. Its type is also RCl, the same as AgCl, NaCl, KCl, &c., and silver in many compounds resembles, and is even isomorphous with, sodium, so that this again justifies their being brought together. Silver chloride, cuprous chloride, and sodium chloride crystallise in the regular system. Besides which, the specific heats of copper and silver require that they should have the atomic weights ascribed to them. To the oxides Cu_2O and Ag_2O there are corresponding sulphides Ag_2S and Cu_2S. They both occur in nature in crystals of the rhombic system, and, what is most important, copper glance contains an isomorphous mixture of them both, and retains the form of copper glance with various proportions of copper and silver, and therefore has the composition R_2S where R = Cu, Ag.

Notwithstanding the resemblance in the atomic composition of the cuprous compounds, CuX, and silver compounds, AgX, with the compounds of the alkali metals KX, NaX, there is a considerable degree of difference between these two series of elements. This difference is clearly seen in the fact that the alkali metals belong to those elements which combine with extreme facility with oxygen, decompose water, and form the most alkaline bases; whilst silver and copper are oxidised with difficulty, form less energetic oxides, and do not decompose water, even at a rather high temperature; they even displace hydrogen from very few acids. The difference between them is also seen in the dissimilarity of the properties of many of the

with cupric sulphate, $CuSO_4,5H_2O$, but if there be a large amount of zinc (or magnesium, iron, nickel, or cobalt) then the form (rhombic or monoclinic) is nearly the same as that of zinc sulphate, $ZnSO_4,7H_2O$. Supersaturated solutions of each of these salts crystallise in that form and with that amount of water which is contained in a crystal of one or other of the salts brought in contact with the solution (Vol. I. p. 591, Note 27).

corresponding compounds. Thus cuprous oxide, Cu_2O, and silver oxide, Ag_2O, are insoluble in water; the cuprous and silver carbonates, chlorides, and sulphates are also sparingly soluble in water. The oxides of silver and copper are also easily reduced to metal. This difference in properties is in intimate relation with that difference in the density of the metals which exists in this case. The alkali metals belong to the lightest, and copper and silver to the heaviest, and therefore the distance between the molecules in these metals is very dissimilar—it is greater for the former than the latter (table in Chap. XV.). From the point of view of the periodic law, this difference between copper and silver and such elements of the I. group as potassium and rubidium, is clearly seen from the fact that copper and silver stand in the middle of those large periods (for example, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br) which start with the true metals of the alkalis—that is to say, the analogy and difference between potassium and copper is of the same nature as that between chromium and selenium, or vanadium and arsenic.

Copper is one of the few metals which have long been known in a metallic form. The Greeks and Romans chiefly imported copper from the island of Cyprus—whence its Latin name, *cuprum*. It was known to the ancients before iron, and was used, especially when alloyed with other metals, for arms and domestic utensils. This will be understood from the fact that copper occurs, although rarely, in a *native state*, and is easily extracted from its other natural compounds. Among the latter are the oxygen compounds of copper. When ignited with charcoal, they easily give up their oxygen to it, and yield metallic copper; hydrogen also easily takes up the oxygen from copper oxide when heated. Copper occurs in a native state, sometimes in association with other ores, in many parts of the Urals and in Sweden, and in considerable masses in America, especially round about the great American lakes; and also in Chili, Japan, and China. The oxygen compounds of copper are also of somewhat common occurrence in certain localities; in this respect certain deposits of the Urals are especially famous. The geological period of the Urals (Permian) is characterised for a considerable distribution of copper ores. Copper is met with in the form of *cuprous oxide*, or *suboxide of copper*, Cu_2O, and is then known as *red copper ore*, because it forms red masses which not unfrequently are crystallised in the regular system. It is found much more rarely in the state of *cupric oxide*, CuO, and is then called *black copper ore*. The most common of the oxygenised compounds of copper are the *basic carbonates*, corresponding with the oxides. These compounds are indubitably of aqueous origin, as is seen not only from the fact that

specimens are frequently found of a gradual transition from the metallic, sulphuretted, and oxidised copper into its various carbonates, but also from the presence of water in their composition, and from the laminar, reniform structure which many of them present. In this respect *malachite* is particularly well known; it is used for ornaments, owing to the diversity of the shades of colour presented by the different layers of deposited malachite, and also as a green paint. The composition of malachite corresponds with the basic carbonate containing one molecule of cupric carbonate to one of hydroxide: $CuCO_3,CuH_2O_2$. In this form the copper frequently appears in admixture with various sedimentary rocks, forming large strata, which confirms the aqueous origin of these compounds. There are many such localities in the Perm and other governments bounding the Urals. *Blue carbonate of copper*, or *azurite*, is also often met with in the same localities; it contains the same ingredients as malachite, but in a different proportion, its composition being $CuH_2O_2,2CuCO_3$. Both these substances may be obtained artificially by the action of the alkali carbonates on solutions of cupric salts at various temperatures. These native carbonates are often used for the extraction of copper, all the more as they very readily give metallic copper, evolving water and carbonic anhydride when ignited, and leaving the easily-reducible cupric oxide. Copper is, however, still more often met with in the form of the sulphides. The sulphides of copper generally occur in chemical combination with the sulphides of iron.[3]

[3] The immense quantities of iron pyrites, FeS_2, which are sometimes met with in nature, very often contain a small quantity of copper sulphide, and on burning the iron pyrites for sulphurous anhydride the copper oxide remains in the residue, from which the copper is often extracted by getting it into solution and then precipitating it by the action of metallic iron. For this purpose the whole of the sulphur is not burnt off from the iron pyrites, but a portion is left behind in the ore, which is then slowly ignited (roasted) with access of air. Cupric sulphate is then formed, and is extracted by water; or, what is better and more frequently done, the residue from the roasting of the pyrites is roasted with common salt, and the solution of cupric chloride obtained by lixiviating is precipitated with iron. A far greater amount of copper is obtained from other sulphuretted ores. Among these *copper glance*, Cu_2S, is more rarely met with. It has a metallic lustre, is grey, generally crystalline, and is obtained in admixture with organic matter; so that there is no doubt that its origin is due to the reducing action of the latter on solutions of cupric sulphate. *Variegated copper ore*, which crystallises in octahedra, not unfrequently forms an admixture in copper glance; it has a metallic lustre, and is reddish-brown; it has a superficial play of colours, due to oxidation proceeding on its surface. Its composition is Cu_3FeS_3. But the most common and widely-distributed copper ore is *copper pyrites*, which crystallises in regular octahedra and is often non-crystalline; it has a metallic lustre, a sp. gr. of 4·0, and yellow colour. Its composition is $CuFeS_2$. It must be remarked that the sulphurous ores of copper are oxidised in the presence of water containing oxygen in solution, and form cupric sulphate, blue vitriol, which is easily soluble in water. If this water contains calcium carbonate, then gypsum and cupric carbonate is formed by double decomposition: $CuSO_4+CaCO_3=CuCO_3+CaSO_4$.

The extraction of copper from the acid ores does not present any difficulty, because the copper, when ignited with charcoal and melted, is reduced from the impurities which accompany it. This mode of smelting copper ores is carried on in cupola or cylindrical furnaces, fluxes forming a slag being added to the mixture of ore and charcoal. The smelted copper still contains sulphur, iron, and other metallic impurities, from which it is freed by fusion in reverberatory furnaces, with access of air to the surface of the molten metal, as the iron and sulphur are more easily oxidised than the copper. The iron then separates as oxides, which collect in the slag.[4]

Therefore copper sulphide in the form of different ores must be considered as the primary product, and the many other copper ores as secondary products, formed by water. This is confirmed by the fact that at the present time the water extracted from many copper mines contains cupric sulphate in solution. From this liquid it is easy to extract cupric oxide by the action of lime, or metallic copper by means of iron; the latter is also formed by the action of organic matter and various impurities of water. Hence metallic copper is sometimes found in natural products of the modification of copper sulphide, and is probably deposited by the action of organic matter present in the water.

[4] Rich oxygenised ores of copper are very rare; the sulphur ores are of more common occurrence, but the extraction of the copper from them is much more difficult. The problem here not only consists in the removal of the sulphur, but also in the removal of the iron combined with the sulphur and copper. This is attained by a whole series of operations, after which there still sometimes remains the extraction of the metallic silver which generally accompanies the copper, although in but small quantity. These processes commence with the roasting—*i.e.* calcination—of the ore with access of air, by which means the sulphur is converted into sulphurous anhydride. It should be here remarked that iron sulphide is more easily oxidised than copper sulphide, and therefore the greater part of the iron in the residue from roasting is no longer in the form of sulphide but of oxide of iron. The roasted ore is mixed with charcoal, siliceous fluxes, and smelted in a cupola furnace. The iron then passes into the slag, because its oxide gives an easily-fusible mass with the silica, whilst the copper, in the form of sulphide, is fused and collects under the slag. The greater part of the iron is removed from the mass by this smelting. The resultant *coarse metal* is again roasted in order to remove the greater part of the sulphur from the copper sulphide, and to convert the metal into oxide. The resultant mass is again smelted. These processes are repeated several times, according to the richness of the ore. During these smeltings a portion of the copper is already obtained in a metallic form, because copper sulphide gives metallic copper with the oxide ($CuS + 2CuO = 3Cu + SO_2$). We will not here describe the furnaces used or the details of this process, but the above remarks include the explanation of those chemical processes which are accomplished in the various technical operations which are had recourse to in the process.

Besides the smelting of copper there also exist (and begin to be widely applied) methods for its extraction from solutions in the wet way, as it is called. Recourse is generally had to these methods for poor copper ores. The methods of extraction by the wet way consist in transferring the copper into solution, from which it is separated by means of metallic iron or by other methods (by the action of an electric current). The sulphides are roasted in such a manner that the greater part of the copper is oxidised into cupric sulphate, whilst at the same time the corresponding iron salts are as far as possible decomposed. This process is based on the fact that the copper sulphides absorb oxygen when they are calcined in the presence of air, forming cupric sulphate. The roasted ore is treated with water, to which acid is sometimes added, and after lixiviation the resultant solution containing copper is treated either with metallic iron, or with

Copper is characterised by its red colour, which distinguishes it from all other metals. Pure copper is soft, and may be beaten out by a hammer at the ordinary temperature, and when hot may be rolled into very thin sheets. Extremely thin leaves of copper transmit a green light. The tenacity of copper is also rather great, and after iron it is one of the most durable metals in this respect. Copper wire of 1 millimetre radius only breaks under a weight of 137 kilograms. The specific gravity of copper is 8·8, unless it contains cavities due to the fact that molten copper absorbs oxygen from the air, which is disengaged on cooling, and therefore gives a porous mass whose density is much less. Rolled copper, and also that which is deposited by the electric current, has a comparatively high density. Copper melts at a temperature nearly approaching to a white heat, although below the temperature at which many kinds of cast iron melt. At a high temperature it is converted into vapour, which communicates a green colour to the flame. Both native copper and that cooled from a molten state crystallise in regular octahedra. Copper is not oxidised in dry air at the ordinary temperature, but when calcined it becomes coated with a layer of oxide, and it does not burn even at the highest temperature. Copper, when calcined in air, forms either the red cuprous oxide or the black cupric oxide, according to the temperature and quantity of air supplied. In air at the ordinary temperature, copper—as every one

milk of lime, which precipitates cupric hydroxide from the solution. Poor oxidised ores of copper may be treated with dilute acids in order to obtain the copper oxides in solution, from which the copper is then easily precipitated either by iron or as hydroxide by lime. According to Hunt and Douglas's method, the copper in the ore is converted by calcination into the cupric oxide, which is brought into solution by the action of a mixture of solutions of ferrous sulphate and sodium chloride, because the oxide converts the ferrous chloride into ferric oxide, forming copper chlorides, according to the equation $3CuO + 2FeCl_2 = CuCl_2 + 2CuCl + Fe_2O_3$. The cupric chloride is soluble in water, and the cuprous chloride is dissolved in the solution of sodium chloride, and therefore all the copper passes into solution, from which it is precipitated by iron.

The copper brought into the market often contains small quantities of various impurities. Among these there are generally present iron, lead, silver, arsenic, and sometimes small quantities of oxides of copper. As copper, when mixed with a small amount of foreign substances, loses its tenacity to a certain degree, the manufacture of very thin sheet copper requires the use of Chili copper, which is distinguished for its great softness, and therefore, when it is desired to have pure copper, it is best to take thin sheet copper, like that which is used in the manufacture of cartridges. But the purest copper is electrolytic copper—that is, that which is deposited from a solution by the action of an electric current.

If the copper contains silver, as is often the case, it is used at gold refineries for the precipitation of silver from its solutions in sulphuric acid. Iron and zinc reduce copper, but copper reduces mercury and silver. The precipitate contains not only the silver which was previously in solution, but also all that which was in the copper. The silver solutions in sulphuric acid are obtained in the separation of silver from gold by treating their alloys with sulphuric acid, which only dissolves the silver.

knows—becomes coated with a brown layer of oxides or a green coating of basic salts, due to the action of the damp air containing carbonic acid. If this action continue for a prolonged time, the copper is covered with a thick coating of basic carbonate, or the so-called verdigris (the *ærugo nobilis* of ancient statues). This is due to the fact that copper, although scarcely capable of oxidising by itself,[5] *in the presence of water and acids*—even very feeble acids, like the carbonic acid—*absorbs oxygen from the air and forms salts*, which is a very characteristic property of it (and of lead). *Copper does not decompose water*, and does not disengage hydrogen from it either at the ordinary or at high temperatures. So also copper does not liberate hydrogen from the oxygen acids, which act on it in two ways: they either give up a portion of their oxygen, forming lower grades of oxidation, or else only react in the presence of air. Thus, when nitric acid acts on copper it evolves nitric oxide, the copper being oxidised at the expense of the nitric acid. So also copper converts sulphuric acid into the lower grade of oxidation—into sulphurous anhydride, SO_2. In these cases, the copper is oxidised into copper oxide, which combines with the excess of acid taken, and therefore forms a cupric salt, CuX_2. Dilute nitric acid does not act on copper, even at the ordinary temperature, but when heated it reacts with great ease; but dilute sulphuric acid does not act on copper unless it have access to air.[6]

[5] Schützenberger showed that when the basic carbonate of copper is decomposed by an electric current it gives, besides the ordinary copper, an allotropic form which grows on the negative platinum electrode, if its surface be less than the positive copper electrode, in the form of brittle crystalline growths of sp. gr. 8·1. It differs from ordinary copper by its giving not nitric oxide but nitrous oxide when treated with nitric acid, and in being very easily oxidised in air, and covered with red shades of colour. Is not this hydrogenised copper, or copper which has occluded hydrogen?

[6] In the presence of air, even such feeble acids as carbonic acid produce an action on copper; the copper then readily absorbs oxygen and gives cupric oxide, which enters into combination with the acid and forms a copper salt. This is taken advantage of in practice; for instance, by pouring dilute acids over copper turnings on revolving tables in the preparation of copper salts, such as verdigris, or the basic acetate $2C_4H_6CuO_4,CuH_2O_2,5H_2O$, which is so much used as an oil paint (*i.e.* with boiled oil). The capacity of copper for absorbing oxygen in the presence of acids is so great that it is possible by this means (by taking, for example, thin copper shavings moistened with sulphuric acid) to take up all the oxygen from a given volume of air, and this is even employed for the analysis of air.

The combination of copper with oxygen is not only aided by acids but also by alkalis, although cupric oxide does not appear to have an acid character. Alkalis do not act on copper except in the presence of air, when they produce cupric oxide, which does not appear to combine with such alkalis as caustic potash or soda. But the *action of ammonia* is particularly distinct (Vol. I. p. 223, Note 2). In the action of a solution of ammonia not only is oxygen absorbed by the copper, but it also acts on the ammonia, and a definite quantity of ammonia is always acted on simultaneously with the passage of the copper into solution. The ammonia is then converted into nitrous acid, according to the re-

Both the oxides of copper, Cu_2O and CuO, are unacted on by air, and, as has been already mentioned, they both occur in nature. However, in the majority of cases copper is obtained in the form of cupric oxide and its salts—for example, the copper compounds used in practice generally belong to this type. This is due to the fact that the *cuprous compounds absorb oxyyen* from the air and pass into cupric compounds. The cupric compounds may serve as the source for the preparation of cuprous oxide, because many reducing agents are capable of deoxidising the oxide into the suboxide. Organic substances are most generally employed for this purpose, and especially saccharine substances, which are able, in the presence of alkalis, to undergo oxidation at the expense of the oxygen of the cupric oxide, and to give acids which combine with the alkali: $2CuO - O = Cu_2O$. In this case, the deoxidation of the copper may be carried further and metallic copper be obtained, if only the reaction be aided by heat. Thus, for example, a fine powder of metallic copper may be obtained by heating an ammoniacal solution of cupric oxide with caustic potash and grape sugar. But if the reducing action of the saccharine substance proceed in the presence of a sufficient quantity of alkali, and at not too high a temperature and in solution, then cuprous oxide is obtained. To see this reaction clearly, it is not sufficient to take any cupric salt, because the alkali neces-

action: $NH_3 + O_3 = NHO_2 + H_2O$, and the nitrous acid thus formed passes into the state of ammonium nitrite, NH_4NO_2. In this manner three equivalents of oxygen are expended on the oxidation of the ammonia, and six equivalents of oxygen pass over to the copper, forming six atoms of cupric oxide. The latter does not remain in the state of oxide, but combines with the ammonia.

A strong solution of common salt does not act on copper, but a dilute solution of the salt corrodes copper, converting it into oxychloride—that is, in the presence of air. This action of salt water is evident in those cases where the bottom of ships are coated with sheet copper. From what has been said above it will be evident that copper vessels should not be employed in the preparation of food, because this contains salts and acids which act on copper in the presence of air, and give copper salts, which are poisonous, and therefore the food prepared in untinned copper vessels may be poisonous. Hence tinned vessels are employed for this purpose—that is, copper vessels coated with a thin layer of tin, on which acid and saline solutions do not act.

Copper, besides the cuprous oxide, Cu_2O, and cupric oxide, CuO, gives two known peroxide forms of oxidation, but they have barely been investigated, and even their composition is not well known. *Copper dioxide* (CuO_2, or CuO_2,H_2O, perhaps $CuHO_2$) is obtained by the action of hydrogen peroxide on cupric hydroxide, when the green colour of the latter is changed into yellow. It is very unstable, and is even decomposed by boiling water, with the evolution of oxygen, whilst the action of acids gives cupric salts, oxygen being also disengaged. A still higher *copper peroxide* is formed by heating a mixture of caustic potash, nitre, and metallic copper to a red heat, and by dissolving cupric hydroxide in solutions of the hypochlorites of the alkali metals. A slight heating of the soluble salt formed is enough for it to be decomposed into oxygen and copper dioxide, which is precipitated. Judging from Frémy's researches, the composition of the copper-potassic compound should be K_2CuO_4. Perhaps this is a compound of peroxides of potassium, K_2O_2, and of copper, CuO_2 (see Chapter XX. Notes 62-64).

sary for the reaction might precipitate cupric oxide—it is necessary to previously add some substance which will prevent this precipitation. Among such substances, tartaric acid, $C_4H_6O_6$, is one of the best. In the presence of a sufficient quantity of tartaric acid, any amount of alkali may be added to a solution of cupric salt without producing a precipitate, because a soluble double salt of cupric oxide and alkali is then formed. If glucose be added to such an alkaline tartaric solution, and the temperature be slightly raised, it first gives a yellow precipitate (this is cuprous hydroxide, CuHO), and then, on boiling, a red precipitate of (anhydrous) cuprous oxide. If such a mixture be left for a long time at the ordinary temperature, it deposits well-formed crystals of anhydrous cuprous oxide belonging to the regular system.[7]

[7] Colourless solutions of cuprous salts may also be obtained by the action of sulphurous or phosphorous acid and like lower grades of oxidation on the blue solutions of the cupric salts. This is very clearly and easily accomplished by means of sodium thiosulphate, $Na_2S_2O_5$, which is oxidised by the process. Cuprous oxide can not only be obtained by the deoxidation of cupric oxide, but also directly from metallic copper itself, because the latter, in oxidising at a red heat in air, first gives cuprous oxide. It is prepared in this manner on a large scale by heating sheet copper rolled into spirals in reverberatory furnaces. It must be seen that the air is not in great excess, and that the coating of red cuprous oxide formed does not begin to pass into the black cupric oxide. If the oxidised spiral sheet is then unbent, the brittle cuprous oxide falls away from the soft metal. The suboxide obtained in this manner fuses with ease. It is necessary to prevent the access of air during the fusion, and if the mass contains cupric oxide it must be mixed with charcoal, which reduces the latter. Cuprous chloride, CuCl, corresponding with cuprous oxide (as sodium chloride corresponds with sodium oxide), when calcined with sodium carbonate, gives sodium chloride and cuprous oxide, carbonic anhydride being evolved, because it does not combine with the cuprous oxide under these conditions. The reaction can be expressed by the following equation: $2CuCl + Na_2CO_3 = Cu_2O + 2NaCl + CO_2$. The cupric oxide itself, when calcined with finely-divided copper (this copper powder may be obtained by many means; for instance, by immersing zinc in a solution of a copper salt, or by igniting cupric oxide in hydrogen), gives the fusible cuprous oxide: $Cu + CuO = Cu_2O$. Both the native and artificial cuprous oxide has a sp. gr. of 5·6. It is insoluble in water, and is not acted on by (dry) air. When heated with acids the suboxide forms a solution of a cupric salt and metallic copper; for example, $Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O$. However, strong hydrochloric acid does not separate metallic copper on dissolving cuprous oxide, which is due to the fact that the cuprous chloride formed is soluble in strong hydrochloric acid. Cuprous oxide also dissolves in a solution of ammonia, and, in the absence of air, gives a colourless solution, which turns blue in the air, absorbing oxygen, owing to the conversion of the cuprous oxide into cupric oxide. The blue solution thus formed may be again reconverted into a colourless cuprous solution by immersing a copper strip in it, because the metallic copper then deoxidises the cupric oxide in the solution into cuprous oxide. Cuprous oxide is characterised by the fact that it gives red glasses when fused with glass or with salts forming vitreous alloys. Glass tinted with cuprous oxide is used for ornaments. The access of air must be avoided during its preparation, because the colour then becomes green, owing to the formation of cupric oxide which colours glass blue. This may even be taken advantage of in testing for copper under the blow-pipe by heating the copper compound with borax in the flame of a blow-pipe; a red glass is obtained in the reducing flame,

Cupric chloride, $CuCl_2$, when ignited, gives *cuprous chloride*, CuCl —*i.e.* the salt corresponding with suboxide of copper—and therefore cuprous chloride is always formed whenever copper enters into reaction with chlorine at a high temperature. Thus, for example, when copper is calcined with mercuric chloride, it forms cuprous chloride and vapours of mercury. The same substance is obtained on heating metallic copper in hydrochloric acid, hydrogen being disengaged; but this reaction only proceeds with finely-divided copper, as hydrochloric acid acts very feebly on compact masses of copper, and, in the presence of air, gives cupric chloride. The green solution of cupric chloride is decolorised by metallic copper, cuprous chloride being formed; but this reaction is only accomplished with ease when the solution is very concentrated and in the presence of an excess of hydrochloric acid, because the latter dissolves the cuprous chloride. The addition of water to the solution precipitates the cuprous chloride because it is less soluble in dilute than in strong hydrochloric acid. Many reducing agents which are able to take up half the oxygen from cupric oxide are able, in the presence of hydrochloric acid, to form cuprous chloride. Stannous salts, sulphurous anhydride, alkali sulphites, phosphorous and hypophosphorous acids, and many similar reducing agents, act in this manner. The usual method of preparing cuprous chloride consists in passing sulphurous anhydride into a very strong solution of cupric chloride: $2CuCl_2 + SO_2 + H_2O = 2CuCl + 2HCl + H_2SO_4$. Cuprous chloride forms colourless cubic crystals which are insoluble in water. It is easily fusible, and even volatile. Under the action of oxidising agents, it passes into the cupric salt, and it absorbs oxygen from moist air, forming cupric oxychloride, Cu_2Cl_2O. *Aqueous ammonia* easily *dissolves* cuprous chloride as well as cuprous oxide; the solution also turns blue on exposure to the air. Thus an ammoniacal solution of cuprous chloride serves as an excellent absorbent for oxygen; but this solution absorbs not only oxygen, but also certain other gases—for example, carbonic oxide and acetylene.[8]

and a blue glass in the oxidising flame, owing to the conversion of the cuprous into cupric oxide.

Etard (1882), by passing sulphurous anhydride into a solution of cupric acetate, obtained a white precipitate of cuprous sulphite, Cu_2SO_3,H_2O, whilst he obtained the same salt, of a red colour, from the double salt of sodium and copper; but there are not any convincing proofs of isomerism in this case.

[8] The solubility of cuprous chloride in ammonia is due to the formation of compounds between the ammonia and the chloride. In a warm solution the compound $NH_3,2CuCl$ is formed, and at the ordinary temperature $CuCl,NH_3$. This salt is soluble in hydrochloric acid, and then forms a corresponding double salt of cuprous chloride and ammonium chloride. By the action of a certain excess of ammonia on a hydrochloric acid solution of cuprous chloride, very well formed crystals, having the composition

When copper is oxidised with a considerable quantity of oxygen at a high temperature, or at the ordinary temperature in the presence of acids, and also when it decomposes acids, converting them into lower grades of oxidation (for example, when submitted to the action of nitric and sulphuric acids), it forms *cupric oxide*, CuO, or, in the presence of acids, cupric salts. Copper rust, or that black mass which forms on the surface of copper when it is calcined, consists of cupric oxide. The coating of the oxidised copper is very easily separated from the metallic copper, because it is brittle and very easily peels off when it is struck or immersed in water. Anhydrous cupric oxide is very easily dissolved in acids, forming cupric salts, CuX_2. They are analogous to the salts MgX_2, ZnX_2, NiX_2, FeX_2, in many respects.

$CuCl,NH_3,H_2O$, are obtained. Cuprous chloride is not only soluble in ammonia and hydrochloric acid, but it also dissolves in solutions of certain other salts—for example, in sodium chloride, potassium chloride, sodium thiosulphate, and certain others. All the solutions of cuprous chloride act in many cases as very powerful deoxidising substances, so, for example, it is easy, by means of these solutions, to precipitate gold from its solutions in a metallic form, according to the equation $AuCl_3 + 3CuCl = Au + 3CuCl_2$.

Among the other compounds corresponding with cuprous oxide, *cuprous iodide*, CuI, is worthy of remark. It is a colourless substance which is insoluble in water and sparingly soluble in ammonia (like silver iodide), but capable of absorbing it, and in this respect it resembles cuprous chloride. It is remarkable from the fact that it is exceedingly easily formed from the corresponding cupric compound CuI_2. A solution of cupric iodide easily decomposes into iodine and cuprous iodide, even at the ordinary temperature, whilst cupric chloride only suffers a similar change on ignition. If a solution of a cupric salt be mixed with a solution of potassium iodide the cupric iodide formed immediately decomposes into free iodine and cuprous iodide, which separates out as a precipitate. In this case the cupric salt acts in an oxidising manner, like, for example, nitrous acid, ozone, and other substances which liberate iodine from iodides, but with this difference, that it only liberates half, whilst they set free the whole of the iodine from potassium iodide: $2KI + CuCl_2 = 2KCl + CuI + I$.

It must also be remarked that cuprous oxide, when treated with hydrofluoric acid, gives an insoluble cuprous fluoride, CuF. Cuprous cyanide is also insoluble in water, and is obtained by the addition of hydrocyanic acid to a solution of cupric chloride saturated with sulphurous anhydride. This cuprous cyanide, like silver cyanide, gives a double soluble salt with potassium cyanide. The double cyanide of copper and potassium is rather stable in the air, and enters into double decompositions with various other salts, like those double cyanides of iron with which we are already acquainted.

Copper hydride, CuH, also belongs to the number of the cuprous compounds. It was obtained by Würtz by mixing a hot (70°) solution of cupric sulphate with a solution of hypophosphorous acid, H_3PO_2. The addition of the reducing hypophosphorous acid must be stopped when a brown precipitate makes its appearance, and when gas begins to be evolved. The brown precipitate is the hydrated cuprous hydride. When gently heated it disengages hydrogen; it gives cuprous oxide when exposed to the air, burns in a stream of chlorine, and liberates hydrogen with hydrochloric acid: $CuH + HCl = CuCl + H_2$. Zinc, silver, mercury, lead, and many other heavy metals do not form such a compound with hydrogen, neither under these circumstances nor under the action of hydrogen at the moment of the decomposition of salts by a galvanic current. The greatest resemblance is seen between cuprous hydride and the hydrogen compounds of potassium, sodium, and platinum—a fact which is not void of interest, owing to the proximity of these metals in the periodic system.

Cupric oxide may be obtained by igniting the nitrate or carbonate of copper. On adding potassium or ammonium hydroxide to a solution of a cupric salt, it forms a gelatinous blue precipitate of the hydrated oxide of copper, CuH_2O_2, insoluble in water. The resultant precipitate *is redissolved by an excess of ammonia*, and gives a very beautiful azure blue solution, of so intense a colour that the presence of small traces of cupric salts may be discovered by this means.[9] An excess of potassium or sodium hydroxide does not dissolve cupric hydroxide. The addition of alkalis to a solution of cupric salts is only attended with the formation of a precipitate of the hydroxide when the solution of the salt is

[9] Cupric oxide and many of its salts are able to give definite, although unstable, *compounds with ammonia*. This faculty already shows itself in the fact that cupric oxide, as well as the salts of copper, dissolves in aqueous ammonia, and also in the fact that salts of copper absorb ammonia gas. If ammonia be added to a solution of any cupric salt, it first forms a precipitate of cupric hydroxide, which then dissolves in an excess of ammonia. The solution thus formed, when evaporated or on the addition of alcohol, frequently deposits crystals of salts containing both the elements of the salt of copper taken and of ammonia. Several such compounds are generally formed. Thus cupric chloride, $CuCl_2$, according to Deherain, forms four compounds with ammonia—namely, one molecule of cupric chloride is able to give crystalline compounds with one, two, four, and six molecules of ammonia. Thus, for example, if ammonia gas be passed into a boiling saturated solution of cupric chloride, then on cooling there separate out small octahedral crystals of a blue colour, containing $CuCl_2,2NH_3,H_2O$. At 150° this substance loses half the ammonia and all the water contained in it, leaving the compound $CuCl_2,NH_3$. Nitrate of copper forms the compound $Cu(NO_3)_2,2NH_3$. This compound remains unchanged on evaporation. Dry cupric sulphate absorbs ammonia gas, and gives a compound containing five molecules of ammonia to one of sulphate (Vol. I. p. 254). If this compound is dissolved in aqueous ammonia, on evaporation it deposits a crystalline substance containing $CuSO_4,4NH_3,H_2O$. At 150° this substance loses the molecule of water and one-fourth of its ammonia. On ignition all these compounds part with the remaining ammonia in the form of an ammoniacal salt, so that the residue consists of cupric oxide. Both the hydrated and anhydrous cupric oxide is soluble in aqueous ammonia.

The solution obtained by the action of aqueous ammonia and air on copper turnings (Note 6) is remarkable for its faculty *of dissolving cellulose*, which is insoluble in water, dilute acids, and alkalis. Paper soaked in such a solution acquires the property of not rotting, of being difficultly combustible, and waterproof, &c. It has therefore been applied, especially in England, to many practical purposes—for example, to the construction of temporary buildings, for covering roofs, &c. The composition of the substance held in solution is $Cu(HO)_2,4NH_3$.

If dry ammonia gas be passed over cupric oxide heated to 265°, a portion of the oxide of copper remains unaltered, whilst the other portion gives *copper nitride*, the oxygen of the copper oxide combining with the hydrogen and forming water. The oxide of copper which remains unchanged is easily removed by washing the resultant product with aqueous ammonia. Copper nitride is very stable, and is insoluble; it has the composition Cu_3N, and is an amorphous green powder, which is decomposed when strongly ignited, and gives cuprous chloride and ammonium chloride when treated with hydrochloric acid. Like the other nitrides copper nitride, Cu_3N, has scarcely been investigated, although it would be very important to become acquainted with the fundamental properties of these compounds for the purpose of characterising the compounds of nitrogen. It is clear from the above composition that the copper in copper nitride occupies the place of hydrogen, and acts like a univalent metal—that is, the nitride corresponds with cuprous oxide.

taken at the ordinary temperature. A hot solution gives a black precipitate of the anhydrous oxide instead of the blue precipitate, and the precipitate of the hydroxide of copper becomes granular, and turns black when the solution is heated. This is due to the fact that the blue hydroxide is exceedingly unstable, and when slightly heated it loses the elements of water and gives the black anhydrous cupric oxide : $CuH_2O_2 = CuO + H_2O$.

Cupric oxide fuses at a strong heat, and on cooling forms a heavy crystalline mass, which is black, opaque, and somewhat tenacious. It is a feebly energetic base, so that not only do the oxides of the metals of the alkalis and alkaline earths displace it from its compounds, but even such oxides as those of lead and silver precipitate it from solutions, which is partially due to these oxides being soluble, although slightly so, in water. However, cupric oxide, and especially the hydroxide, easily combines with even the least energetic acids, and does not give any compounds with bases ; but, on the other hand, *it easily forms basic salts*, and in this respect outstrips magnesium and recalls the oxides of lead or mercury. Therefore the hydroxide of copper dissolves in solutions of neutral cupric salts. The cupric salts are generally blue or green, because cupric hydroxide itself is coloured. But some of the salts are colourless in the anhydrous state.[10]

[10] The normal *cupric nitrate*, $CuN_2O_6,3H_2O$, is obtained as a deliquescent and soluble (in alcohol) salt of a blue colour by dissolving copper or cupric oxide in nitric acid. It is so easily decomposed by the action of heat that it is impossible to drive off the water of crystallisation from it, as it begins to decompose, leaving cupric oxide, before the water comes off. During the ignition of the normal salt the cupric oxide formed enters into combination with the remaining undecomposed normal salt, and gives a basic salt, $CuN_2O_6,2CuH_2O_2$. The same basic salt is obtained if a certain quantity of alkali or cupric hydroxide or carbonate be added to the solution of the normal salt, which is even decomposed when boiled with metallic copper, and forms the basic salt as a green powder, which easily decomposes under the action of heat and leaves a residue of cupric oxide. The basic salt, having the composition $CuN_2O_6,3CuH_2O_2$, is nearly insoluble in water.

The normal *carbonate of copper*, $CuCO_3$, occurs in nature, although extremely rarely. If solutions of cupric salts be mixed with solutions of alkali carbonates, then, as in the case of magnesium, carbonic anhydride is evolved and basic salts are formed, which vary in composition according to the temperature and conditions of the reaction. By mixing cold solutions, a voluminous blue precipitate is formed, containing an equivalent proportion of cupric hydroxide and carbonate (after standing or heating, its composition is the same as malachite; sp. gr., 3·5): $2CuSO_4 + 2Na_2CO_3 + H_2O = CuCO_3,CuH_2O_2 + 2Na_2SO_4 + CO_2$. If the resultant blue precipitate is heated in the liquid, it loses water and is transformed into a granular green mass of the composition Cu_2CO_4—*i.e.* into a compound of the normal salt with anhydrous cupric oxide. This salt of the oxide corresponds with orthocarbonic acid, $C(OH)_4 = CH_4O_4$, where 4H is replaced by 2Cu. On further boiling, this salt loses a portion of the carbonic acid, forming black cupric oxide, so unstable is the compound of copper with carbonic anhydride. Another basic salt which occurs in nature, $2CuCO_3,CuH_2O_2$, is known as azurite, or blue carbonate of copper; it also loses carbonic acid when boiled with water. On mixing a solution of cupric sulphate

The commonest normal salt is *blue vitriol—i.e.* the normal cupric sulphate. It generally contains five molecules of water of crystallisation, $CuSO_4,5H_2O$. It forms the product of the action of strong sulphuric acid on copper, sulphurous anhydride being evolved. The same salt is obtained in practice by carefully roasting sulphuretted ores of copper, and also by the action of water holding oxygen in solution on them : $CuS+O_4=CuSO_4$. This salt forms a bye-product, obtained at gold refineries, when the silver is precipitated from the sulphuric acid solution by means of copper. It is also obtained by pouring dilute sulphuric acid over sheet copper in the presence of air, or by heating cupric oxide or carbonate in sulphuric acid. The crystals of this salt belong to the triclinic system, have a specific gravity of 2·19, are of a beautiful blue colour, and give a solution of the same colour. 100 parts of water at 0° dissolve 15, at 25° 23, and at 100° about 45 parts of cupric sulphate, $CuSO_4$. At 100° this salt loses four molecules of water of crystallisation, retaining only one molecule, which it only parts with at a high temperature (220°), and then gives a white powder of the anhydrous sulphate ; and the latter, on further calcination, loses the elements of sulphuric anhydride, leaving cupric oxide, like all the cupric salts. The anhydrous (colourless) cupric sulphate is sometimes used for absorbing water ; it turns blue in the process. It offers the advantage that it retains both hydrochloric acid and water, but not carbonic anhydride. Cupric sulphate is used for steeping seed corn ; this is said to prevent the growth of certain parasites on the plants. In practice, a considerable quantity of cupric sulphate is also used in the preparation of other copper salts—for instance, of certain pigments—and a particularly large quantity is used *in the galvanoplastic process*, which consists in the deposition of copper from a solution of cupric sulphate by the action of a galvanic current, when the metallic copper is deposited on the negative pole and takes the form of the latter. The description of the processes of galvanoplastic art introduced by Yakobi in St. Petersburg forms a part of applied physics, and will not be touched on here ; and we will only mention that, although first introduced for small articles, it is now used for such articles as type moulds (*clichés*), for maps, prints, &c., and also for large statues, and for the deposition of iron, zinc, nickel, gold, silver, &c., on other metals and materials. The beginning of the application of the galvanic current to the practical extraction of metals from solutions has also been since established, especially since

with sodium sesquicarbonate no precipitate is at first obtained, but after boiling a precipitate is formed having the composition of malachite. Debray artificially obtained azurite by heating cupric nitrate with chalk.

the dynamo-electric machines of Gramme, Siemens, and others have rendered it possible to cheaply convert the mechanical movement of the steam engine into an electric current. One must think that the application of the electric current, which has long since given such important results in chemistry, will, in the near future, play an important part in technical processes, the example being shown by electric lighting.[11]

The alloys of copper with certain metals, and especially with zinc and tin, are easily formed by directly melting the metals together. They are easily cast into moulds, forged, and worked like copper, whilst they are much more durable in the air, and are therefore frequently used in the arts. Even the ancients exclusively used alloys of copper, not pure copper but its alloys with tin or different kinds of bronze (Chapter XVIII.). The alloys of copper with zinc are called *brass* or 'yellow metal.' Brass contains about 32 p.c. of zinc; generally, however, it does not contain more than 65 p.c. of copper. The remainder is composed of lead and tin, which usually occur, although in small quantities, in brass. Yellow metal contains about 40 p.c. of zinc. The addition of zinc to copper changes its colour to a considerable degree; with a certain amount of zinc the colour of the copper becomes yellow, and with a still larger proportion of zinc an alloy is formed which has a greenish tint. In those alloys of zinc and copper which contain a greater amount of zinc than of copper, the yellow colour disappears and is replaced by a greyish colour. But when the amount of zinc is diminished to about 15 p.c., the alloy is red and hard, and is called 'tombac.' A contraction takes place in alloying copper with zinc, so that the volume of the alloy is less than that of either metal individually. The zinc volatilises on prolonged heating at a high temperature, and metallic copper remains behind. When heated in the air, the zinc oxidises before the copper, so that all the zinc alloyed with copper may be removed from the copper by this means. An important property of brass containing about 30 p.c. of zinc is that it is soft and malleable in the cold, but becomes somewhat brittle when heated. We may also mention that ordinary copper money contains,

[11] Commercial blue vitriol generally contains ferrous sulphate. The salt is purified by converting the ferrous salt into a ferric salt by heating the solution with chlorine or nitric acid. The solution is then evaporated to dryness, and the unchanged cupric sulphate extracted from the residue, which will contain the larger portion of the ferric oxide. The remainder will be separated if cupric hydroxide is added to the solution and boiled; the cupric oxide, CuO, then precipitates the ferric oxide, Fe_2O_3, just as it is itself precipitated by silver oxide. But the solution will contain a small proportion of a basic salt of copper, and therefore sulphuric acid must be added to the filtered solution, and the salt then crystallised. Acid salts are not formed, and cupric sulphate itself has an acid reaction on litmus paper.

for the sake of rendering it hard, tin, zinc, and iron (Cu = 59 p.c.); that it is now customary to add a small amount of phosphorus to copper and bronze, for the same purpose; that copper is added to silver and gold in coining, &c., also to render it hard; that in Germany, Switzerland, and Belgium, and other countries, a silver-white alloy (melchior, German silver, &c.), for base coinage and other purposes, is prepared from brass and nickel (from 10 to 20 p.c. of nickel; 20 to 30 p.c. zinc; 50 to 70 p.c. copper), or directly from copper and nickel, or, more rarely, from an alloy containing silver, nickel, and copper.[11b]

Copper, in its cuprous compounds, is so analogous to *silver*, that were there no cupric compounds, or if silver gave stable compounds of the higher oxide, AgO, the resemblance would be as close as that between chlorine and bromine or zinc and cadmium; but silver compounds corresponding to AgO are quite unknown. Although silver peroxide—which was regarded as AgO, but which Berthelot (1880) recognised as the trioxide Ag_2O_3—is known, still it does not form any true salts, and consequently cannot be placed along with cupric oxide. In distinction to copper, silver as a metal does not oxidise under the influence of heat; and its oxides, Ag_2O and Ag_2O_3, easily lose oxygen.[12] Silver does *not oxidise* in air at the ordinary pressure, and is therefore classed among the so-called *noble metals*. It has a white colour, which is much purer than that of any other known metal, especially when it is chemically pure. In practice silver is used alloyed, because chemically-pure silver is so soft that it is exceedingly easily worn, whilst, when fused with a small amount of copper, it becomes very hard, without losing its colour.[13]

[11b] Ball (also Kamensky), 1888, by investigating the electrical conductivity of the alloys of antimony and copper with lead, came to the conclusion that there only exist two definite compounds of antimony and copper, whilst the other alloys are either alloys of these two together or with antimony or with copper. These compounds are Cu_2Sb and Cu_4Sb—one corresponds with the maximum, and the other with the minimum, electrical resistance. In general, the resistance offered to an electrical current forms one of the methods by which the composition of definite alloys (for example, Pb_2Zn_7) is often established, whilst the electromotive force of alloys affords (Laurie, 1888) a still more accurate method. Thus the alloys Zn_2Cu and Cu_3Sn were shown to be such that the electromotive force varied distinctly on their formation.

[12] Cupric oxide is also able to dissociate when heated. Debray and Joannis showed that it then evolves oxygen, whose maximum tension is constant at a given temperature if fusion does not ensue (cupric oxide dissolves in fused cuprous oxide), and this loss of oxygen results in the formation of cuprous oxide, and on cooling the oxygen is all reabsorbed and cupric oxide again formed.

[13] There are not many soft metals; lead, tin, copper, silver, iron, and gold are somewhat soft, and potassium and sodium very soft. The metals of the alkaline earths are already sonorous and hard, and many other metals are even brittle, especially bismuth and antimony. But the very slight significance which these properties have in

Silver occurs *in nature*, both in a native state and in certain compounds. Native silver, however, is of rather rare occurrence. A far

determining the fundamental chemical properties of substances (although, however, of immense importance in the practical applications of metals) is seen from the example shown by zinc, which is hard at the ordinary temperature, soft at 100°, and brittle at 200°.

As the value of silver depends exclusively on its purity, and as there is no possibility of telling the amount of impurities alloyed with it from its external appearance, it is customary in most countries to mark an article with the amount of pure silver it contains after an accurately-made analysis known as the assay of the silver. In France the assay of silver shows the amount of pure silver in 100 parts by weight; in Russia the amount of pure silver in 96 parts—that is, the assay shows the number of zolotniks (4·26 grams) of pure silver in one pound (410 grams) of alloyed silver. Russian silver is generally 84 assay—that is, contains 84 parts by weight of pure silver and 12 parts of copper and other metals. French money contains 90 p.c. (in the Russian system this will be 86·4 assay) by weight of silver [English coins and jewellery contain 92·5 p.c. of silver]; the silver rouble is of 83⅓ assay—that is, it contains 86·8 p.c. of silver—and the smaller Russian silver coinage is of 48 assay, and therefore contains 50 p.c. of silver. Silver ornaments and articles are usually made in Russia of 84 and 72 assay silver. As the alloys of silver and copper, especially after being subjected to the action of heat, are not so white as pure silver, they generally undergo a process known as 'blanching' (or 'pickling') after being worked up. This consists in removing the copper from the surface of the article by subjecting it to a dark-red heat and then immersing it in dilute acid. During the calcination the copper on the surface is oxidised, whilst the silver remains unchanged; the dilute acid then dissolves the copper oxides formed, and pure silver is left on the surface. The surface is dull after this treatment, owing to the removal of a portion of the metal by the acid. After being polished the article acquires the desired lustre and colour, so as to be indistinguishable from a pure silver object. In order to test a silver article, a portion of its mass must be taken, not from the surface, but to a certain depth. The methods of assay used in practice are very varied. The commonest and most often used is that known as *cupellation*. It is based on the difference in the oxidisability of copper, lead, and silver. The cupel is a porous cup with thick sides, made by compressing

FIG. 95.—Cupel for silver assaying.

FIG. 96.—Clay muffle.

bone ash. The porous mass of bone ash absorbs the fused oxides, especially the lead oxide, which is easily fusible, but it does not absorb the unoxidised metal. The latter collects into a globule under the action of a strong heat in the cupel, and on cooling solidifies into a button, which may then be weighed. Several cupels are placed in a muffle. A muffle is a semi-cylindrical clay vessel, shown in the accompanying drawing. The sides of the muffle are pierced with several orifices, which allow the access of air into it. The muffle is placed in a furnace, where it is strongly heated. Under the action of the air entering into the muffle the copper of the silver alloy is oxidised, but as the oxide of copper is infusible, or, more strictly speaking, difficultly fusible, a certain quantity of lead is added to the alloy; the lead is also oxidised by the air at the high temperature of the muffle, and gives the very fusible lead oxide. The copper oxide then fuses with the lead oxide,

greater quantity of silver occurs in combination with sulphur, and especially in the form of *silver sulphide*, Ag_2S, with lead sulphide or copper sulphide, or the ores of various other metals. The largest amount of silver is extracted from the lead in which it occurs. If this lead be calcined in the presence of air, it oxidises, and the resultant lead oxide, PbO ('litharge' or 'silberglätte,' as it is called), melts into a mobile liquid, which is easily removed. The silver remains in an unoxidised metallic state.[14] This process is called *cupellation*.

and is absorbed by the cupel, whilst the silver remains as a bright white globule. If the weight of the alloy taken and of the silver left on the cupel be determined, it is possible to calculate the composition of the alloy. Hence the essence of cupellation consists in

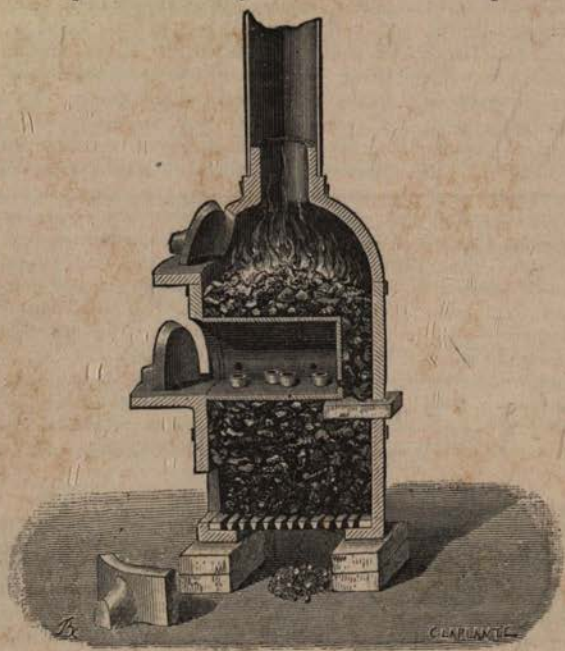


FIG. 97.—Portable muffle furnace.

the separation of the oxidisable metals from silver, which does not oxidise under the action of heat. A more accurate method, based on the precipitation of silver from its solutions in the form of silver chloride, is described in detail in works upon analytical chemistry.

[14] In America, whence the largest amount of silver is now obtained, they work ores containing not more than $\frac{1}{8}$ p.c. of silver, whilst at $\frac{1}{2}$ p.c. its extraction is very profitable. Moreover, the extraction of silver from ores containing not more than 0·01 p.c. of this metal is sometimes profitable. The majority of the lead smelted from galena contains silver, which is extracted from it. Thus near Arras, in France, they work an ore which contains about 65 parts of lead and 0·088 parts of silver in 100 parts of ore, which corresponds with 136 parts of silver in 100000 parts of lead. At Freiberg, in Saxony, they

Commercial silver generally contains copper, and, more rarely, also other metallic impurities. Chemically *pure silver* is obtained either by cupellation or by subjecting ordinary silver to the following treatment. The silver is first dissolved in nitric acid, which converts it and the

work an ore (enriched by mechanical dressing) containing about 0·9 of silver, 160 of lead, and 2 of copper in 10000 parts. In every case the lead is first extracted in the manner described in Chapter XVIII., and this lead will hold all the silver. Not unfrequently other ores of silver are mixed with lead ores, in order to obtain an argentiferous lead as the product. The extraction of small quantities of silver from lead is facilitated by the fact (Pattinson's process) that the molten argentiferous lead in cooling first deposits crystals of pure lead, which fall to the bottom of the cooling vessel, whilst the proportion of silver in the unsolidified mass increases according to the removal of the crystals of lead. The lead is enriched in this manner up to a contents of $\frac{1}{400}$ part of silver, and is then subjected to cupellation on a larger scale.

The ores of silver which contain a larger amount of it are: silver glance, Ag_2S (sp. gr. 7·2); argentiferous-copper glance, CuAgS; horn silver or chloride of silver, AgCl; argentiferous grey copper ore; polybasite, M_9RS_6 (where M = Ag, Cu, and R = Sb, As), and argentiferous gold. The latter is the usual form in which gold is found in alluvial deposits and ores. The crystals of gold from the Berezoffsky mines in the Urals contain 90 to 95 of gold and 5 to 9 of silver, and the Altai gold contains 50 to 65 of gold and 36 to 38 of silver. The proportion of silver in native gold varies between these limits in other localities. Silver ores, which generally occur in veins, usually contain native silver and various sulphur compounds. The most famous mines in Europe are in Saxony (Freiberg), which has a yearly output of up to 26 tons of silver, Hungary, and Bohemia (41 tons). In Russia, silver is extracted in the Altai and at Nerchinsk (17 tons). The richest silver mines known are in America, especially in Chili (up to 70 tons), Mexico (200 tons), and more particularly in the western states of North America. The richness of these mines may be judged from the fact that one mine in the State of Nevada (Comstock, near Washoe and the cities of Gold Hill and Virginia), which was discovered in 1859, gave an output of 400 tons in 1866. The modes of extracting silver from lead and argentiferous ores are mainly of two kinds—cupellation and chlorination. The first method is applied to the extraction of silver from argentiferous lead. The mode of cupellation on a large scale does not differ from the assay on a small scale (Note 13); it is based on the property of silver of not oxidising in air when heated, whilst the lead and other metals present are oxidised and give fusible oxides, which are easily removed from the silver. In general, the object in the extraction of silver is to convert it into an alloy with lead, which is easily freed from the silver by cupellation. The method of chlorination consists in converting the silver in an ore into silver chloride. This is either done by a wet or a dry method. When the silver chloride is formed, the extraction of the metal is also done by two methods. The first consists in the silver chloride being reduced to metal by means of iron, and, mercury being added to the mass, the mercury dissolves the silver, but does not act on the other metals. The mercury holding the silver in solution is distilled, when the silver remains behind. This method is called *amalgamation*. The other method is less used, and consists in dissolving the silver chloride in sodium chloride or in sodium thiosulphate, and then precipitating the silver from the solution—by means of iron, for example. In America the chlorination is carried on simultaneously with the amalgamation, but we shall not describe this method, all the more as another process is usually employed in Europe, in which the two processes are carried on separately; the chlorination being done by roasting the ore containing silver with common salt. The salt in volatilising acts on the compounds of silver, and converts them into silver chloride. The amalgamation is then carried on in rotating barrels containing the roasted ore mixed with water, iron, and mercury. The iron reduces the silver chloride by taking up the chlorine from it. The technical details of these processes are described in works on metallurgy.

copper into nitrates, $Cu(NO_3)_2$ and $AgNO_3$; hydrochloric acid is then added to the resultant green (owing to the presence of the cupric salt) solution, which is considerably diluted with water in order to retain the lead chloride in solution if the silver contained lead. The copper and many other metals remain in solution, whilst the silver is precipitated as silver chloride. The precipitate is allowed to settle, and the liquid is decanted off; the precipitate is then washed and fused with sodium carbonate. A double decomposition then takes place, sodium chloride and silver carbonate being formed; but the latter decomposes into metallic silver, because the silver oxide is decomposed by heat: $Ag_2CO_3 = Ag_2 + O + CO_2$. The silver chloride may also be mixed with metallic zinc, sulphuric acid, and water, and left for a certain time, when the zinc removes the chlorine from the silver chloride and precipitates the silver as a powder. This finely-divided silver is called 'molecular silver.'[15]

Chemically-pure silver has an exceeding pure white colour, and a specific gravity of 10·5. In fusing it contracts, and therefore a piece of silver floats on the molten metal. The fusing-point of silver is about 950° C., and at the high temperature attained by the combustion of detonating gas it volatilises. By employing silver reduced from silver chloride by milk sugar and caustic potash, and distilling it, Stas obtained silver purer than that obtained by other means; in fact, this was perfectly pure silver. The vapour of silver has a very beautiful green colour, which is seen when a silver wire is placed in an oxyhydrogen flame.[16]

As regards the capacity of silver for chemical reactions, it is remarkable, in this respect, for its small capacity for combination with

[15] There is another practical method which is also suitable for separating the silver from the solutions obtained in photography, and consists in precipitating the silver by oxalic acid. In this case the amount of silver in the solution must be known, and 23 grams of oxalic acid dissolved in 400 grams of water must be added for every 60 grams of silver in solution in a litre of water. A precipitate of silver oxalate, $Ag_2C_2O_4$, is then obtained, which is insoluble in water but soluble in acids. Therefore, if the liquid contain any free acid it must be previously freed from it by the addition of sodium carbonate. The resultant precipitate of silver oxalate is dried, mixed with an equal weight of dry sodium carbonate, and thrown into a gently-heated crucible. The separation of the silver then proceeds without an explosion, while the silver oxalate if heated alone decomposes with explosion.

According to Stas, the best method of obtaining silver from its solutions is by the reduction of silver chloride dissolved in ammonia by means of an ammoniacal solution of cuprous thiosulphate; the silver is then precipitated in a crystalline form. A solution of ammonium sulphite may be used instead of the cuprous salt.

[16] In melting, silver absorbs a considerable amount of oxygen, which is disengaged on solidifying. One volume of molten silver absorbs up to 22 volumes of oxygen. In solidifying, the silver forms cavities like the crater of a volcano, and throws off metal, owing to the evolution of the gas; all these phenomena recall a volcano on a miniature

oxygen and for its considerable energy for combination with sulphur, iodine, and certain kindred non-metals. *Silver does not oxidise*[17] at any temperature, and its oxide, Ag_2O, is decomposed by heat.

It is also a very important fact that silver is not oxidised by oxygen either in the presence of alkalis, even at exceedingly high temperatures, or in the presence of acids—at least, of dilute acids—which renders it a very important metal in chemical practice for the preservation and fusion of alkalis, and also for many purposes in everyday life. Ozone, however, oxidises it.

Of all acids nitric acid evinces the greatest *action* on silver. The reaction is accompanied by the formation of oxides of nitrogen and silver nitrate, $AgNO_3$, which dissolves in water and does not, therefore, hinder the further action of the acid on the metal. The halogen acids, especially hydriodic acid, act on silver, hydrogen being evolved; but this action soon stops, owing to the halogen compounds of silver being insoluble in water and very slightly soluble in acids; they therefore preserve the remaining mass of metal from the further action of the acid; in consequence of this the action of the halogen acids is only distinctly seen with finely-divided silver. Sulphuric acid acts on silver in the same manner that it does on copper, only it must be concentrated and at a higher temperature. Sulphurous anhydride, and not hydrogen, is then evolved, but there is no action at the ordinary temperature, even in the presence of air. Among the various salts, sodium chloride (in the presence of moisture, air, and carbonic

scale (Dumas). Silver which contains a small quantity of copper or gold, &c., does not show this property of dissolving oxygen.

Stas showed that silver is oxidised by air in the presence of acids. V. d. Pfordten confirmed this, and showed that an acidified solution of potassium permanganate rapidly dissolves silver in the presence of air.

Silver is very malleable and ductile; it may be beaten into leaves 0·002 mm. in thickness. Silver wire may be made so fine that 1 gram is drawn into a wire 2½ kilometres long. In this respect silver is only second to gold. A wire of 2 mm. diameter breaks under a strain of 20 kilograms.

[17] The absorption of oxygen by molten silver is, however, an oxidation, but it is at the same time a phenomenon of solution. Twenty-two cubic centimetres of oxygen are capable of being dissolved in one cubic centimetre of molten silver, and even if it be calculated as having a temperature of 0°, it only weighs 0·03 grams, whilst 1 cubic centimetre of silver weighs at least 10 grams, and therefore it is impossible to suppose that the absorption of the oxygen is attended with the formation of any definite compound (rich in oxygen) of silver and oxygen (about 45 atoms of silver to 1 of oxygen) in any other but a dissociated form, and this is the state in which substances in solution must be regarded (Chapter I.).

Le Chatelier showed that at 300° and 15 atmospheres pressure silver absorbs so much oxygen that it may be regarded as having formed the compound Ag_4O, or a mixture of Ag_2 and Ag_2O. And silver oxide, Ag_2O, only decomposes at 300° under low pressures, whilst at pressures above 10 atmospheres there is no decomposition at 300° but only at 400°.

acid) and potassium cyanide (in the presence of air) act on silver more clearly than any others, converting it into silver chloride and a double cyanide respectively.

Although silver does not directly combine with oxygen, still three different grades of combination with oxygen may be obtained indirectly from the salts of silver. They are all, however, unstable, and decompose into oxygen and metallic silver when ignited. These three oxides of silver have the following composition: *silver suboxide*, Ag_4O,[18] corresponding with (the little investigated) suboxides of the alkali metals; *silver oxide*, Ag_2O, corresponding with the oxides of the alkali metals, and the ordinary salts of silver, AgX; and *silver peroxide*, AgO,[19] or, judging from Berthelot's researches, Ag_2O_3. *Silver oxide* is obtained as a brown precipitate (which when dried does not contain water) by adding potassium hydroxide to a solution of a silver salt—for example, of silver nitrate. The precipitate formed seems, however, to be an hydroxide, AgHO. The reaction of the alkali on the solution of the salt may be supposed to be $AgNO_3+KHO=KNO_3+AgHO$, and the formation of the anhydrous oxide, $2AgHO=Ag_2O+H_2O$, may be compared with the formation of the anhydrous cupric oxide by the action of potassium hydroxide on hot cupric

[18] Silver suboxide (Ag_4O) or argentous oxide is obtained from argentic citrate by heating it to 100° in a stream of hydrogen. Water and argentous citrate are then formed, and the latter, although but slightly soluble in water, gives a reddish-brown solution. When boiled, this solution becomes colourless and deposits metallic silver, the argentic salt being again formed. Wöhler, who discovered this oxide, obtained it as a black precipitate by adding potassium hydroxide to the above solution of argentous citrate. With hydrochloric acid the suboxide gives a brown compound, Ag_2Cl. The same compound is obtained by the action of light on the higher chloride. Other acids do not combine with silver suboxide, but convert it into an argentic salt and metallic silver. This is also the character of other suboxides. In this respect cuprous oxide presents a certain resemblance with these suboxides. But copper forms a suboxide of the composition Cu_4O, which is obtained by the action of an alkaline solution of stannous oxide on cupric hydroxide, and is decomposed by acids into cupric salts and metallic copper. The problems offered by the suboxides, as well as by the peroxides, cannot be considered as fully explained.

[19] *Silver peroxide*, AgO or Ag_2O_3, is obtained by the decomposition of a dilute (10 p.c.) solution of silver nitrate by the action of a galvanic current. On the positive pole, where oxygen is usually evolved in the decomposition of salts, brittle grey needles, with a metallic lustre and which sometimes attain a rather considerable size, are then formed. They are insoluble in water, and decompose with the evolution of oxygen when they are dried and heated, especially up to 150°, and, like lead dioxide, barium peroxide, &c., their action is strongly oxidising. When treated with acids, oxygen is evolved and a salt formed. Hence, for instance, silver peroxide absorbs sulphurous anhydride and forms silver sulphate. Hydrochloric acid evolves chlorine; ammonia reduces the silver, and is itself oxidised, forming water and gaseous nitrogen. Analyses of the above-mentioned crystals show that they contain silver nitrate, peroxide, and water. According to Fisher, they have the composition $4AgO,AgNO_3,H_2O$, and, according to Berthelot, $4Ag_2O_3,2AgNO_3,H_2O$.

solutions. This shows that the silver hydroxide decomposes into water and silver oxide, even at low temperatures; at least the hydroxide no longer exists at 60°, but forms the anhydrous oxide. Silver oxide is almost insoluble in water; but, nevertheless, it is undoubtedly a rather powerful basic oxide, because it displaces the oxides of many metals from their soluble salts, and saturates such acids as nitric acid, forming with them neutral salts, which do not act on litmus paper. Undoubtedly, water dissolves a small quantity of silver oxide, which explains the possibility of its action on solutions of salts—for example, on solutions of cupric salts. Water in which silver oxide is shaken up has a distinctly alkaline reaction. The oxide is distinguished by its great instability when heated, so that it loses all its oxygen when slightly heated. Hydrogen reduces it at about 80°.[20] The feebleness of the affinity of silver for oxygen is shown by the fact that silver oxide decomposes under the action of light, so that it must be kept in opaque vessels. The silver *salts* are colourless and decompose when heated, leaving metallic silver if the elements of the acid are volatile. They have a peculiar metallic taste, and are exceedingly poisonous; the majority of them are acted on by light, especially in the presence of organic substances, which are then oxidised. The alkaline carbonates give a white precipitate of silver carbonate, Ag_2CO_3, which is insoluble in water, but soluble in ammonia and ammonium carbonate. Aqueous ammonia, added to a solution of a normal silver salt, first acts like potassium hydroxide, but the precipitate dissolves in an excess of the reagent, like the precipitate of cupric hydroxide.[21] Silver oxalate and the halogen compounds of silver are insoluble in water, and hydrochloric acid and soluble chlorides give,

[20] According to Müller, ferric oxide is reduced by hydrogen (see Chap. XXII. Note 5) at 295° (into what?), cupric oxide at 140°, Ni_2O_3 at 150°; nickelous oxide, NiO, is reduced to the suboxide, Ni_2O, at 195°, and to nickel at 270°; zinc oxide requires so high a temperature for its reduction that the glass tube in which Müller conducted the experiment did not stand the heat; antimony oxide requires a temperature of 215° for its reduction; yellow mercuric oxide is reduced at 130° and the red oxide at 230°; silver oxide at 85°, and platinum oxide even at the ordinary temperature.

[21] If a solution of a silver salt is precipitated by sodium hydroxide, and aqueous ammonia is added drop by drop until the precipitate is completely dissolved, then the liquid when evaporated deposits a violet mass of crystalline silver oxide. If moist silver oxide be left in a strong solution of ammonia it gives a black mass, which easily decomposes with a loud explosion, especially when struck. This black substance is called fulminating silver. Probably this is a compound like the other compounds of oxides with ammonia, and in exploding the oxygen of the silver oxide probably forms water with the hydrogen of the ammonia, which is naturally accompanied by the evolution of heat and formation of gaseous nitrogen. Fulminating silver is also formed when potassium hydroxide is added to a solution of silver nitrate in ammonia. The dangerous explosions which are produced by this compound render it needful that great care be taken when salts of silver come into contact with ammonia and alkalis.

as has been already repeatedly observed, a white precipitate of silver chloride in solutions of silver salts. Potassium iodide gives a yellowish precipitate of silver iodide. Zinc separates all the silver in a metallic form from solutions of silver salts. Many other metals and reducing agents—for example, organic substances—also reduce silver from the solutions of its salts.

Silver nitrate, $AgNO_3$, is known by the name of lunar caustic (or *lapis infernalis*); it is obtained by dissolving metallic silver in nitric acid. If the silver be impure, the resultant solution will contain a mixture of the nitrates of copper and silver. If this mixture be evaporated to dryness and the residue be carefully fused at an incipient red heat, then all the cupric nitrate is decomposed, whilst the greater part of the silver nitrate remains unchanged. On treating the fused mass with water the latter is dissolved, whilst the cupric oxide remains insoluble. If a certain amount of silver oxide be added to the solution containing the nitrates of silver and copper, it displaces all the cupric oxide. In this case it is naturally not necessary to take pure silver oxide, but only to pour off some of the solution and to add potassium hydroxide to one portion, and to mix the resultant precipitate of the hydroxides, $Cu(OH)_2$ and AgOH, with the remaining portion.[22] By these methods all the copper can be easily removed and

[22] So that we here encounter the following phenomena: copper displaces silver from the solutions of its salts, and silver oxide displaces copper oxide from cupric salts. Guided by the conceptions enunciated in Chap. XV., we can account for this in the following manner. The atomic volume of silver = 10·3, and of copper = 7·2, of silver oxide = 32, and of copper oxide = 13. A greater contraction has taken place in the formation of cupric oxide, CuO, than in the formation of silver oxide, Ag_2O, because in the former (13 − 7 = 6) the volume after combination with the oxygen has increased by very little, whilst the volume of silver oxide is considerably greater than that of the metal it contains [32 − (2 × 10·3) = 11·4]. Hence silver oxide is less compact than cupric oxide, and is therefore less stable than it; but, on the other hand, there are greater intervals between the atoms in silver oxide than in cupric oxide, and hence silver oxide is able to give more stable compounds than those of copper oxide. This is verified by the figures and data of their reactions. Unfortunately it is impossible to calculate for cupric nitrate, because this salt has not yet been obtained in an anhydrous state; but the sulphates of both oxides are known. The specific gravity of copper sulphate in an anhydrous state is 3·53, and of silver sulphate 5·36; the molecular volume of the former is 45, and of the latter 58. We will now compare these volumes with those of the oxides. The group SO_3 in the copper occupies, as it were, a volume 45 − 13 = 32, and in the silver salt a volume 58 − 32 = 26; hence a smaller contraction has taken place in the formation of the copper salt from the oxide than in the formation of the silver salt, and consequently the latter should be more stable than the former. Therefore the silver oxide is able to decompose the salt of copper oxide, whilst with respect to the metals both salts have been formed with an almost identical contraction, because 58 volumes of the silver salt contain 21 volumes of metal (difference = 37), and 45 volumes of the copper salt contain 7 volumes of copper (difference = 38). Besides which, it must be observed that copper oxide displaces iron oxide, just as silver oxide displaces copper oxide. Silver, copper, and iron, in the form of oxides, displace each other in the above order, but in the form of metals in a reverse order

silver nitrate obtained, which may be ultimately purified by crystallisation. It crystallises in colourless transparent prismatic plates, which are not acted on by air. They are anhydrous. Its sp. gr. is 4·34; it dissolves in an equal weight of water at the ordinary temperature, and in half its weight of boiling water. The pure salt is not acted on by light, but it easily acts in an oxidising manner on the majority of organic substances, which it generally blackens. This is due to the fact that the organic substance is oxidised by the silver nitrate, which is reduced to metallic silver; this is then obtained in a finely-divided state, which causes the black stain. This is taken advantage of for marking linen. Silver nitrate is for the same reason used for *cauterising wounds* and various growths on the body. It then acts in virtue of its oxidising capacity in destroying the organic matter, which it oxidises, as is seen from the separation of a coating of black metallic powdery silver from the part cauterised. It may be remarked that the black stain produced by the reduction of metallic silver disappears under the action of a solution of mercuric chloride or of potassium cyanide, because these salts act on finely-divided silver. From the description of the preparation of silver nitrate it will have been seen that this salt fuses without decomposition at an incipient red heat, and when cast into sticks it is usually employed for cauterising. On further heating, the fused salt undergoes decomposition, first forming silver nitrite and then metallic silver. With ammonia, silver nitrate forms, on evaporation of the solution, colourless crystals containing $AgNO_3,2NH_3$. In general the salts of silver, like cuprous, cupric, zinc, &c., salts, are able to give several compounds with ammonia; for example, silver nitrate in a dry state absorbs three molecules. The ammonia is generally easily expelled from these compounds by the action of heat.

Silver nitrate under the action of water and a halogen gives nitric acid, a halogen salt of silver, and a silver salt of an oxygen acid of the halogen. Thus, for example, a solution of chlorine in water, when mixed with a solution of silver nitrate, gives silver chloride and chlorate. It is here evident that the reaction of the silver nitrate is identical with the reaction of the caustic alkalis, as the nitric acid is all set free and the silver oxide only reacts in exactly the same manner

(iron, copper, silver). The cause of this order of the displacement of the oxides lies, amongst other things, in their composition. They have the composition Ag_2O, Cu_2O_2, Fe_2O_3; the oxide containing the less proportion of oxygen displaces that containing a larger proportion, because the basic character diminishes with the increase of contained oxygen.

Copper also displaces mercury from its salts. It may here be remarked that Spring (1888), on leaving a mixture of dry mercurous chloride and copper for two hours, observed a distinct reduction, which belongs to the number of those phenomena which demonstrate the existence of a mobility of parts (*i.e.* atoms and molecules) in solid substances.

as aqueous potash acts on free chlorine. Therefore the reaction may be expressed in the following manner: $6AgNO_3+3Cl_2+3H_2O=5AgCl+AgClO_3+6NHO_3$.

Silver nitrate, like the nitrates of the alkalis, does not contain any water of crystallisation. Moreover, the other salts of silver almost always separate out without any water of crystallisation. The silver salts are further characterised by the fact that they *give neither basic nor acid salts*, owing to which the formation of silver salts generally forms the means of determining the true composition of acids.

Silver gives insoluble and exceedingly stable compounds *with the halogens*. They are obtained by double decomposition with great facility whenever a silver salt comes into contact with halogen salts. Solutions of nitrate, sulphate, and all other kindred salts of silver give a precipitate of silver chloride or iodide in solutions of chlorides and iodides and of the halogen acids, because the halogen salts of silver are insoluble both in water [23] and in other acids. *Silver chloride*, AgCl, is then obtained as a white flocculent precipitate, silver bromide forms a yellowish precipitate, and silver iodide has a very distinct yellow colour. These halogen compounds sometimes occur in nature; they are formed by a dry method—by the action of halogen compounds on silver compounds, especially under the influence of heat. Silver chloride easily fuses at 451° on cooling from a molten state; it forms of a rather soft horn-like mass, which can be cut with a knife, and is therefore known as *horn silver*. It volatilises at a higher temperature. Its ammoniacal solution, on the evaporation of the ammonia, deposits crystalline chloride of silver, in octahedra. Bromide and iodide of silver also appear in forms of the regular system, so that in

[23] Silver chloride is almost perfectly insoluble in water, but is somewhat soluble in water containing sodium chloride or hydrochloric acid, or other chlorides, and many salts, in solution. Thus at 100° 100 parts of water saturated with sodium chloride dissolve 0·4 parts of silver chloride. Bromide and iodide of silver are less soluble in this respect, as also in regard to other solvents. It should be remarked that *silver chloride dissolves in solutions of ammonia, potassium cyanide, and of sodium thiosulphate*, $Na_2S_2O_5$. Silver bromide is almost perfectly analogous to the chloride, but silver iodide is nearly insoluble in a solution of ammonia. Silver chloride even absorbs dry ammonia gas, forming very unstable ammoniacal compounds. When heated these compounds (Vol. I. p. 247, Note 8) evolve the ammonia, as they also do under the action of all acids. Silver chloride enters into double decomposition with potassium cyanide, forming a soluble double cyanide, which we shall presently describe; it also forms a double soluble salt, $NaAgS_2O_3$, with sodium thiosulphate.

Silver chloride offers different modifications in the structure of its molecule, as is seen in the variations in the consistency of the precipitate, and in the differences in the action of light. Stas and Carey Lea investigated this subject, which has a particular importance in photography, because silver bromide also gives *photo-salts*.

this respect the halogen salts of silver resemble the halogen salts of the alkali metals.[24]

[24] *Silver bromide* and *iodide* resemble the chloride in many respects, but the degree of affinity of silver for iodine is greater than that for chlorine and bromine. Deville deduced this fact from a number of experiments. Thus silver chloride, when treated with hydriodic acid, evolves hydrochloric acid, and forms silver iodide. Finely-divided silver easily liberates hydrogen when treated with hydriodic acid; it produces the same decomposition with hydrochloric acid, but in a considerably less degree and only on the surface. The difference between silver chloride and iodide is especially remarkable, because the formation of the former is attended with a greater contraction than that of the latter. The volume of AgCl = 26; of chlorine 27, of silver 10, the sum = 37, hence a contraction has ensued; and in the formation of silver iodide an expansion takes place, because the volume of Ag is 10, of I 26, and of AgI 39 (density, AgCl, 5·59; AgI, 5·67), instead of 36. The atoms of chlorine have united with the atoms of silver without moving asunder, whilst the atoms of iodine must have moved apart in combining with the silver. The matter presents itself differently with respect to the metal; the distance between its atoms in the metal = 2·2, in silver chloride = 3·0, and in silver iodide = 3·5; hence its atoms have moved asunder considerably in both cases. It is also very remarkable that Fizeau observed that the density of silver iodide increases with a rise of temperature—that is, a contraction takes place when it is heated and an expansion when it is cooled.

In order to explain the fact that in silver compounds the iodide is more stable than the chloride and oxide, Professor N. N. Beketoff, in his 'Researches on the Phenomena of Substitutions' (Kharkoff, 1865), proposed the following original hypothesis, which we will give in almost the words of the author:—In the case of aluminium, the oxide, Al_2O_3, is more stable than the chloride, Al_2Cl_6, and the iodide, Al_2I_6. In the oxide the amount of the metal is to the amount of the element combined with it as 54·8 (Al = 27·4) is to 48, or in the ratio 112 : 100; for the chloride the ratio is = 25 : 100; for the iodide it = 7 : 100. In the case of silver the oxide (ratio = 1350 : 100) is less stable than the chloride (ratio = 304 : 100), and the iodide (ratio of the weight of metal to the weight of the halogen = 85 : 100) is the most stable. From these and similar examples it is seen that the most stable compounds are those in which the weights of the combined substances are equal. This may be partly explained by the attraction of like molecules even after their having passed into combination with others. This attraction is proportional to the product of the acting masses. In silver oxide the attraction of Ag, for $Ag_2 = 216 \times 216 = 46656$, and the attraction of Ag_2 for $O = 216 \times 16 = 3456$. The attraction of like molecules thus counteracts the attraction of the unlike molecules. The former naturally does not overcome the latter, otherwise there would be a disruption, but it nevertheless diminishes the stability. In the case of an equality or proximity of the magnitude of the combining masses, the attraction of the like parts will counteract the stability of the compound to the least extent—in other words, with an inequality in the combined masses, the molecules have an inclination to return into an elementary state, to decompose, which does not exist to such an extent where the combined masses are equal. There is, therefore, a tendency for large masses to combine with large, and for small masses to combine with small. Hence $Ag_2O + 2KI$ gives $K_2O + 2AgI$. In double decomposition or substitution, the weight of atoms has the preponderating influence, because they are not accompanied by a great change of volumes, and if there is a change it is a contraction, which is very frequently seen in the formation of insoluble compounds (Cremers), the possibility of whose formation determines many such reactions, as Berthollet demonstrated. The influence of an equality of masses on the stability is seen particularly clearly in the effect of a rise of temperature. Argentic, mercuric, or auric oxides, and such like oxides, composed of unequal masses, are decomposed by heat, whilst the oxides of the light metals (like water) are not so easily decomposed by heat. Silver chloride and iodide approach the condition of equality, and are not decomposed by heat. The most stable oxides

Silver chloride may be decomposed, with the separation of silver oxide, by heating it with a solution of an alkali, and if an organic

under the action of heat are those of magnesium, calcium, silicon, and aluminium, which approach the condition of equality. For this reason also hydriodic acid decomposes with greater facility than hydrochloric acid. Chlorine does not act on magnesia or alumina, but it acts on lime and silver oxide, &c. This is partially explained by the fact that by taking heat as movement, and knowing that the atomic heats of the free elements are equal, it must be supposed that the amount of the movement of atoms (their *vis viva*) is equal, and as it is equal to the product of the mass (atomic weight) into the square of the velocity, it follows that the greater the combining weight the smaller will be the velocity (more correctly, its square), and if the combining weights be nearly equal, then the velocities will also be nearly equal. Therefore, the greater the difference between the weights of the combined atoms the greater will the difference between their velocities be. The difference between the velocities will increase with the temperature, and therefore the temperature of decomposition will be the sooner attained the greater be the original difference—that is, the greater the difference of the weights of the combined substances. The nearer these weights are to each other, the more analogous the movement of the unlike atoms, and, consequently, the more stable the resultant compound.

The instability of cupric chloride or nitric oxide, the absence of compounds of fluorine with oxygen, whilst there are compounds of oxygen with chlorine, the greater stability of the oxygen compounds of iodine than of chlorine, the stability of boron nitride, and the instability of cyanogen, and a number of like instances, where, judging from the above argument, one would expect (owing to the nearness of the atomic weights) a stability, show that Beketoff's addition to the mechanical theory of chemical phenomena is still far from sufficient for explaining the true relations of affinities. Nevertheless, in his mode of explaining the relative stabilities of compounds we find an exceedingly interesting treatment of questions of primary importance. Without such efforts it would be impossible to generalise the complex data of experimental knowledge.

Silver cyanide, AgCN, is closely analogous to the haloid salts of silver. It is obtained, in similar manner to silver chloride, by the addition of potassium cyanide to silver nitrate. A white precipitate is then formed, which is almost insoluble in boiling water. It is also, like silver chloride, insoluble in dilute acids. However, it is dissolved when heated with nitric acid, and both hydriodic and hydrochloric acids act on it, converting it into silver chloride and iodide. But alkalis do not act on silver cyanide, although they act on the other haloid salts of silver. Ammonia and solutions of the cyanides of the alkali metals dissolve silver cyanide, as they do the chloride. In the latter case double cyanides are formed—for example, $KAgC_2N_2$. This salt is obtained in a crystalline state on evaporating a solution of silver cyanide in potassium cyanide. It is much more stable than silver cyanide itself. It has a neutral reaction, does not change in the air, and does not smell of hydrocyanic acid. Many acids, in acting on a solution of this double salt, precipitate the insoluble silver cyanide. Metallic silver dissolves in a solution of potassium cyanide in the presence of air, with formation of the same double salt and potassium hydroxide, and when silver chloride dissolves in potassium cyanide it forms potassium chloride, besides the salt $KAgC_2N_2$. This double salt of silver is used in silver plating. For this purpose potassium cyanide is added to its solution, as otherwise silver cyanide, and not metallic silver, is deposited by the electric current. If two electrodes—one positive (silver) and the other negative (copper)—be immersed in such a solution, then silver will be deposited upon the latter, and the silver of the positive electrode will be dissolved by the liquid, which will thus preserve the same amount of metal in solution as it originally contained. If instead of the negative electrode a copper object be taken, well cleaned from all dirt, then the silver will be deposited in an even coating; this, indeed, forms the mode of *silver plating by the wet method*, which is most often used in practice. A solution of one part of silver nitrate in 30 to 50 parts of water, and mixed with a sufficient quantity of a solution of

substance be added to the alkali the chloride can be easily reduced to metallic silver, the silver oxide being reduced in the oxidation of the organic substance. Iron, zinc, and many other metals reduce silver chloride in the presence of water. Cuprous and mercurous chlorides and many organic substances are also able to reduce the silver from chloride of silver. This shows the rather easy decomposability of the halogen compounds of silver. Silver iodide is much more stable in this respect than the chloride. The same is also observed with respect to the *action of light*. The colourless silver chloride soon acquires a violet colour when exposed to the action of light, and especially under the direct action of the sun's rays. Silver chloride after being acted upon by light is no longer entirely soluble in ammonia, but leaves metallic silver undissolved, from which it might be thought that the

potassium cyanide to redissolve the precipitate of silver cyanide formed, gives a dull coating of silver, but if twice as much water be used the same mixture gives a bright coating.

Silver plating in the wet way has now replaced to a considerable extent the old process of *dry silvering*, because this process, which consists in dissolving silver in mercury and applying the amalgam to the surface of the objects, and then vaporising the mercury, offers the great disadvantage of the poisonous mercury fumes. Besides these, there is another method of silver plating, based on the direct displacement of silver from its salts by other metals—for example, by copper. The copper reduces the silver from its compounds, and the silver separated is deposited upon the copper. Thus a solution of silver chloride in sodium thiosulphate deposits a coating of silver upon a strip of copper immersed in it. It is best for this purpose to take pure *silver sulphite*. It is prepared by mixing a solution of silver nitrate with an excess of ammonia, and adding a saturated solution of sodium sulphite and then alcohol, which precipitates silver sulphite from the solution. The latter and its solutions are very easily decomposed by copper. Metallic iron produces the same decomposition, and iron and steel articles may be very readily silver-plated by means of the thiosulphate solution of silver chloride. Indeed, copper and similar metals may even be silver-plated by means of silver chloride; if the chloride of silver, with a small amount of acid, be rubbed upon the surface of the copper, it becomes covered with a coating of silver, which it has reduced.

Silver plating is not only applicable to metallic objects, but also to glass, china, &c. Glass is silvered for various purposes—for example, glass globes silvered internally are used for ornamentation, and have a mirrored surface. Common looking-glass silvered upon one side forms a mirror which is better than the ordinary mercury mirrors, owing to the truer colours of its image due to the whiteness of the silver. For optical instruments—for example, telescopes—concave mirrors are now made of silvered glass, which has first been moulded and polished into the required form. The *silvering of glass* is based on the fact that silver which is reduced from certain solutions deposits itself uniformly in a perfectly homogeneous and continuous, but very thin, layer, forming a bright reflecting surface. Certain organic substances have this property of reducing silver in this form. The best known among these are certain aldehydes—for instance, common acetaldehyde, C_2H_4O, which easily oxidises in the air and forms acetic acid, $C_2H_4O_2$. This oxidation also easily proceeds at the expense of silver oxide, when a certain amount of ammonia is added to the mixture. The oxide of silver gives up its oxygen to the aldehyde, and the silver reduced from it is deposited in a metallic state in a uniform bright coating. The same action is produced by certain saccharine substances and certain organic acids, such as tartaric acid, &c.

action of light consisted in the decomposition of the silver chloride into chlorine and metallic silver. Indeed, the silver chloride becomes in time darker and darker. Silver bromide and iodide are much more slowly acted on by light, and, according to certain observations, when pure they are even quite unacted on; at least they do not change in weight, so that if they are acted on by light, the change they undergo must be one of a change in the structure of their parts and not of decomposition, as it is in silver chloride. The silver chloride under the action of light changes in weight, which indicates the formation of a volatile product, and the formation of metallic silver on dissolving in ammonia shows the evolution of chlorine. The latter does actually take place under the action of light, but the decomposition does not go as far as into chlorine and silver, but only to the formation of a sub-chloride of silver, which is of a brown colour and is easily decomposed into metallic silver and silver chloride, $Ag_2Cl = AgCl + Ag$. This change of the chemical composition and structure of the halogen salts of silver under the action of light forms the basis of *photography*, because the halogen compounds of silver, after having been exposed to light, give a precipitate of finely-divided silver, of a black colour, when treated with reducing agents.[25]

The insolubility of the halogen compounds of silver forms the basis of many methods used in chemical practice. Thus by means of this reaction it is possible to obtain salts of other acids from a halogen salt of a given metal. The formation of the halogen compounds of silver is used very frequently in the investigation of organic substances; for example, if any product of metalepsis containing iodine or chlorine be heated with a silver salt or silver oxide, then the silver combines with the halogen and gives a halogen salt, whilst the elements previously combined with the silver replace the halogen. For instance, ethylene dibromide, $C_2H_4Br_2$, is transformed into ethylene diacetate, $C_2H_4(C_2H_3O_2)_2$, and silver bromide by heating it with silver acetate, $2AgO_2C_2H_3$. The insolubility of the halogen compounds of silver is still more frequently taken advantage of in determining the amount of silver and halogen in a given solution. If it is required, for instance, to determine the quantity of chlorine present in the form of a metallic chloride in a given solution, then a solution

[25] In photography these are called 'developers.' The most common developers are: solutions of ferrous sulphate, pyrogallol, ferrous oxalate, hydroxylamine, quinol (its action is particularly good and its use very convenient), potassium sulphite, &c. The chemical processes of photography are of great practical and theoretical interest; but it would be impossible in this work to enter into this special branch of chemistry, which has as yet been very little worked out from a theoretical point of view.

of silver nitrate is added to it so long as it gives a precipitate. On *shaking or stirring* the liquid, the silver chloride easily settles in the form of heavy flakes. It is possible to thus precipitate the whole of the chlorine from a solution, without adding an excess of silver nitrate, because it can be clearly observed whether the addition of a fresh quantity of silver nitrate produces a precipitate in the clear liquid. In this manner it is possible to add to a solution containing chlorine, as much silver as is required for its entire precipitation, and to calculate the amount of chlorine previously in solution from the amount of the solution of silver nitrate consumed, if the quantity of silver nitrate in this solution has been previously determined. The atomic proportions and preliminary experiments with a pure salt—for example, with sodium chloride—will give the amount of chlorine from the quantity of silver nitrate. The details of these methods must be looked for in works on analytical chemistry.

Accurate experiments, and more especially the *researches of Prof. Stas* of Brussels, show the relation which exists between silver and metallic chlorides fully reacting together. These researches have led to the determination of the *combining weights* of silver, sodium, potassium, chlorine, bromine, iodine, and other elements, and are distinguished for their model exactitude, and we will therefore describe them in some detail. As sodium chloride is the chloride most generally used for the precipitation of silver, all the more as it can be easily obtained in a pure state, we will here cite the quantitative observations made by Stas for showing the co-relation between the quantities of chloride of sodium and silver which react together. He first obtained perfectly pure sodium chloride. For this purpose he took pure rock salt, containing only a small quantity of magnesium and calcium compounds and a small amount of potassium salts. This salt was dissolved in water, and the saturated solution evaporated by boiling. The sodium chloride separated out during the boiling, and the mother liquor containing the impurities was poured off. Alcohol of 65 p.c. strength and platinic chloride were added to the resultant salt, in order to precipitate all the potassium and a certain part of the sodium salts. The resultant alcoholic solution, containing the sodium and platinum chlorides, was then mixed with a solution of pure ammonium chloride in order to remove the platinic chloride. After this precipitation, the solution was evaporated in a platinum retort, and then separate portions of this purified sodium chloride were collected as they crystallised. The same salt was prepared from sodium sulphate, tartrate, nitrate, and from the platinochloride, in order to have sodium chloride prepared by different methods and from different sources, and all the samples of

sodium chloride thus prepared were purified and investigated in their relation to silver. After being dried, weighed quantities of all ten samples of sodium chloride were dissolved in water and mixed with a solution in nitric acid of a weighed quantity of perfectly pure silver. A slightly greater quantity of silver was taken than would be required for the decomposition of the sodium chloride, and when, after pouring in all the silver solution, the silver chloride had settled, the amount of silver remaining in excess was determined by means of a solution of sodium chloride of known strength. This solution of sodium chloride was added so long as it formed a precipitate. In this manner was determined how many parts of sodium chloride correspond with 100 parts by weight of silver. The result of ten determinations was that for the entire precipitation of 100 parts of silver from 54·2060 to 54·2093 parts of sodium chloride were required. The difference is so inconsiderable that it has no perceptible influence on the subsequent result of calculation. The mean of ten experiments was that 100 parts of silver react with 54·2078 parts of sodium chloride. In order to learn from this the relation between the chlorine and silver, it was necessary to determine the quantity of chlorine held in 54·2078 parts of sodium chloride, or, what is just the same, the quantity of chlorine which combines with 100 parts of silver. For this purpose Stas made a series of observations on the quantity of silver chloride obtained from 100 parts of silver. Four syntheses were made by him for this purpose. The first synthesis consisted in the formation of silver chloride by the action of chlorine on silver at a red heat. This experiment showed that 100 parts of silver give 132·841, 132·843 and 132·843 of silver chloride. The second method consisted in dissolving a given quantity of silver in nitric acid and precipitating it by means of gaseous hydrochloric acid passed over the surface of the liquid; the resultant mass was evaporated in the dark to drive off the nitric acid and excess of hydrochloric acid, and the remaining silver chloride was fused first in an atmosphere of hydrochloric acid gas and then in air. In this process the silver chloride was not washed, and therefore there could be no loss from solution. Two experiments made by this method showed that 100 parts of silver give 132·849 and 138·848 parts of silver chloride. A third series of determinations was also made on solutions, by precipitating a solution of silver nitrate with a certain excess of gaseous hydrochloric acid. The amount of silver chloride obtained was altogether 132·848. Lastly, a fourth determination was made by precipitating dissolved silver with a solution of ammonium chloride, when it was found that a considerable amount of silver (0·3175) had passed into solution in the washing; for 100 parts

of silver there was obtained altogether 132·8417 of silver chloride. Thus from the mean of seven determinations it appears that 100 parts of silver give 132·8445 parts of silver chloride—that is, that 32·8445 parts of chlorine are able to combine with 100 parts of silver and with that quantity of sodium which is contained in 54·2078 parts of sodium chloride. These observations show that 32·8445 parts of chlorine combine with 100 parts of silver and with 21·3633 parts of sodium. From these figures expressing the relation between the combining weights of chlorine, silver, and sodium, it would be possible to determine their atomic weights—that is, the combining quantity of these elements with respect to one part by weight of hydrogen or 16 parts of oxygen, if there existed a series of similarly accurate determinations for the reactions between hydrogen or oxygen and one of these elements—chlorine, sodium, or silver. If we determine the quantity of silver chloride which is obtained from silver chlorate, $AgClO_3$, we shall know the relation between the combining weights of silver chloride and oxygen, so that, taking the quantity of oxygen as a constant magnitude, we can learn from this reaction the combining weight of silver chloride, and from the preceding numbers the combining weights of chlorine and silver. For this purpose it was first necessary to obtain pure silver chlorate. This was done by Stas by acting on silver oxide or carbonate of silver suspended in water, with gaseous chlorine.[26]

The decomposition of the silver chlorate thus obtained was accomplished by means of the action of a solution of sulphurous anhydride on it. The salt was first fused by carefully heating it at 243°. The solution

[26] This is how he describes the phenomenon which then takes place: if silver oxide or carbonate be suspended in water, and an excess of water saturated with chlorine be added, then all the silver is converted into chloride, just as is the case with oxide or carbonate of mercury, and the water then contains, besides the excess of chlorine, only pure hypochlorous acid without the least trace of chloric or chlorous acid. If a stream of chlorine be passed into water containing *an excess of silver oxide* or silver carbonate, while the liquid is continually shaken, then the reaction is the same as the preceding; silver chloride and hypochlorous acid are formed. But this acid does not long remain in a free state; it gradually acts on the silver oxide and gives silver hypochlorite. If, after some time, the current of chlorine is stopped but the shaking is continued, then the liquid loses its characteristic odour of hypochlorous acid, while preserving its energetic decolorising property, because the silver hypochlorite which is formed is easily soluble in water. In the presence of an excess of silver oxide this salt can be kept for several days without decomposition, but it is exceedingly unstable when there is not an excess of silver oxide or carbonate present. So long as the solution of silver hypochlorite is shaken up with the silver oxide, it preserves its transparency and bleaching property, but directly it is allowed to stand, and the silver oxide settles, it becomes rapidly cloudy and deposits large flakes of silver chloride, so that the black silver oxide which had settled becomes covered with the white precipitate. The liquid then loses its bleaching properties, and contains silver chlorate in solution, which has a slightly alkaline

of sulphurous anhydride used was one saturated at 0°. Sulphurous anhydride in dilute solutions is oxidised at the expense of silver chlorate, even at low temperatures, with great ease if the liquid be continually shaken, sulphuric acid and silver chloride being formed: $AgClO_3 + 3SO_2 + 3H_2O = AgCl + 3H_2SO_4$. After decomposition, the resultant liquid was subjected to evaporation, and the residue of silver chloride was weighed. Thus the process consisted in taking a known weight of silver chlorate, converting it into silver chloride, and determining the weight of the latter. The analysis conducted in this manner gave the following results, which, like the preceding, designate the weight in a vacuum calculated from the weights obtained in air. In the first experiment it appeared that 138·7890 grams of silver chlorate gave 103·9795 parts of silver chloride, and in the second experiment that 259·5287 grams of chlorate gave 194·44515 grams of silver chloride, and after fusion 194·4435 grams. The mean result of both experiments, converted into percentages, shows that 100 parts of silver chlorate contain 74·9205 of silver chloride and 25·0795 parts of oxygen. From this it is possible to calculate the combining weight of silver chloride, because in the decomposition of silver chlorate there are obtained three atoms of oxygen and a combining weight of silver chloride: $AgClO_3 = AgCl + 3O$. Taking the weight of an atom of oxygen to be 16, we find that the combining weight of silver chloride is, judging from the mean result, equal to 143·395. Thus if O=16, AgCl=143·395, and as, judging from the preceding experiments, silver chloride contains 32·8445 parts of chlorine per 100 parts of silver, therefore the weight of the atom of silver will be 107·942 and of chlorine 35·453. The weight of the atom of sodium is determined from the fact that 21·3633 parts of sodium chloride combine with 32·8445 parts of chlorine, and consequently Na=23·0599. This conclusion is

reaction, owing to the presence of a small amount of dissolved oxide. In this manner the reactions which are consecutively accomplished may be expressed by the equations:

$$6Cl_2 + 3Ag_2O + 3H_2O = 6AgCl + 6HClO; \qquad 6HClO + 3Ag_2O = 3H_2O + 6AgClO;$$
$$6AgClO = 4AgCl + 2AgClO_3.$$

Hence, Stas gives the following method for the preparation of silver chlorate. A slow current of chlorine is caused to act on oxide of silver, suspended in water, which is put into a state of continuous movement. The shaking is continued after the supply of chlorine has been stopped, in order that the free hypochlorous acid should pass into silver hypochlorite, and the resultant solution of the hypochlorite is drawn off from the sediment of the excess of silver oxide. This solution decomposes spontaneously into silver chloride and chlorate. The pure silver chlorate, $AgClO_3$, does not change under the action of light. The salt is made ready for further use by drying it in dry air at 150°. It is necessary during drying to prevent the access of any organic matter; this is done by filtering the air through cotton wool, and passing it over a layer of red-hot copper oxide.

obtained by the analysis of silver chlorate. This result was verified by means of the analysis of potassium chlorate by decomposing it by heat and determining the weight of the potassium chloride formed, and also by accomplishing the same decomposition by igniting the chlorate in a stream of hydrochloric acid. The combining weight of potassium chloride was thus determined, and another series of determinations confirmed the relation between chlorine, potassium, and silver, in the same manner as the relation between sodium, chlorine, and silver was determined above. Consequently, the combining weights of sodium, chlorine, and potassium could be deduced by conjoining these data with the analysis of silver chlorate and the synthesis of silver chloride. The agreement between the results showed that the determinations made by the above method were perfectly correct, and did not depend in any considerable degree on the methods which were employed in the preceding determinations, as the combining weights of chlorine and silver obtained were the same as before. There was naturally a difference, but so small a one that it indubitably depended on the errors incidental to every process of weighing and experiment. The combining weight of silver was also established by Stas, by means of the synthesis of silver sulphide and the analysis of silver sulphate. The combining weight obtained by this method was 107·920. The synthesis of silver iodide and the analysis of silver iodate gave the figure 107·928. The synthesis of silver bromide with the analysis of silver bromate gave the figure 107·921. The synthesis of silver chloride and the analysis of silver chlorate gave a mean result of 107·937. Hence there is no doubt that the combining weight of silver is at least as much as 107·9 —greater than 107·90 and less than 107·95. Stas determined the combining weights of many other elements in this manner, such as lithium, potassium, sodium, bromine, chlorine, iodine, and also nitrogen, because the determination of the amount of silver nitrate obtained from a given amount of silver already gives the combining weight of nitrogen. Taking the combining weight of oxygen as 16, he obtained the following combining weights for these elements: nitrogen 14·04, silver 107·93, chlorine 35·46, bromine 79·95, iodine 126·85, lithium 7·02, sodium 23·04, potassium 39·14. These figures differ slightly from those which are usually employed in chemical investigations. They must be regarded as the result of the best observations, whilst the figures usually used in chemical practice are only approximate—they are, so to speak, round numbers for the atomic weights.

The exhaustive investigations conducted by Stas on the atomic weights of the above-named elements have an important significance in the solution of the problems as to whether the atomic weights of the

elements can be expressed in whole numbers if the unit taken be the atomic weight of hydrogen. Proust, in the beginning of this century, stated that this was the case, and held that the atomic weights of the elements are multiples of the atomic weight of hydrogen. The subsequent determinations of Berzelius, Penny, Marchand, Marignac, Dumas, and more especially of Stas, proved this conclusion to be unjustifiable; because, for example, a whole series of elements proved to have fractional atomic weights—for example, chlorine, about 35·5. In virtue of this, Marignac and Dumas stated that the atomic weights of the elements are expressed in relation to hydrogen, either in whole numbers or in numbers with simple fractions of the magnitude $\frac{1}{2}$ and $\frac{1}{4}$. But Stas's researches refute this supposition also. Even between the combining weight of hydrogen and oxygen, there is not, as far as is yet known, judging from the reseaches of Dumas, Erdmann, and others (Vol. I. p. 149), that simple relation which is required by *Proust's hypothesis*.[27]

[27] This hypothesis, for the establishment or refutation of which so many researches have been made, is exceedingly important, and fully deserves the attention which has been given to it. Indeed, if it appeared that the atomic weights of all the elements could be expressed in whole numbers with reference to hydrogen, or if they at least proved to be commensurable with one another, then it could be affirmed with confidence that the elements, with all their diversity, were formed of one material condensed or grouped in various manners into the stable, and, under known conditions, undecomposable groups which we call the atoms of the elements. At first it was supposed that all the elements were nothing else but condensed hydrogen; but when it appeared that the atomic weights of the elements could not be expressed in whole numbers in relation to hydrogen, then it might still be supposed that there exists a certain material from which both hydrogen and all the other elements were formed. If it appeared that four atoms of this material form an atom of hydrogen, then the atom of chlorine would present itself as consisting of 142 atoms of this substance, the weight of whose atom would be equal to 0·25. But in this case the atoms of all the elements should be expressed in whole numbers with respect to the weight of the atom of this original material. Let us suppose that the atomic weight of this material is equal to unity, then all the atomic weights should be expressible in whole numbers relatively to this unit. This atom of one element, let us suppose, would weigh m, and of another n, but, as both m and n must be whole numbers, it follows that the atomic weights of all the elements would be commensurable. But it is sufficient to glance over the results obtained by Stas, and to be assured of their accuracy, especially for silver, in order to, if not entirely destroy, at least strongly undermine, this attractive hypothesis. Therefore we must refuse to be assured of the building up from a single substance of the elements known by us. This assurance is not supported either by any known transformation (because one element has never been converted into another element), nor in the commensurability of the atomic weights of the elements. Although the hypothesis of the formation of all the elements from a single substance (for which Crookes has suggested the name protyle) is most attractive in its comprehensiveness, it cannot be denied nor accepted for want of sufficient data. Marignac endeavoured, however, to overcome Stas's conclusions as to the incommensurability of the atomic weights by supposing that in his, as in the determinations of all other observers, there were unperceived errors which were quite independent of the mode of observation; for example, silver nitrate may be supposed to be an unstable substance which changes, under the heatings, evaporations, and other processes to which it is sub-

Among the platinum metals ruthenium, rhodium, and palladium, by their atomic weights and properties, approach to silver, just as the analogues of iron (iron, cobalt, and nickel) approach in all respects to copper. *Gold* stands in exactly the same position in relation to the

jected in the reactions for the determination of the combining weight of silver. It might be supposed, for instance, that silver nitrate contains some impurity which cannot be removed by any means; it might also be supposed that a portion of the elements of the nitric acid are disengaged in the evaporation of the solution of silver nitrate (owing to the decomposing action of water), and in its fusion, and that we have not to deal with normal silver nitrate, but with a slightly basic salt. In this case the observed combining weight will not refer to an actually definite chemical compound, but to some mixture for which there does not exist any perfectly exact combining relations. Marignac upholds this proposition by the fact that the conclusions of Stas and other observers respecting the combining weights determined with the greatest exactitude very nearly agree with the proposition of the commensurability of the atomic weights. For example, the combining weight of silver was shown to be equal to 107·93, so that it only differs by 0·07 from the whole number 108, which is generally accepted for silver. The combining weight of iodine proved to be equal to 126·85—that is, it differs from 127 by 0·15. The combining weights of sodium, nitrogen, bromine, chlorine, and lithium are still nearer to the whole or round numbers which are generally accepted. But Marignac's proposition will hardly stand criticism. Indeed if we express the combining weights of the elements determined by Stas in relation to hydrogen, then the approximation of these weights to whole numbers disappears, because one part of hydrogen in reality does not combine with 16 parts of oxygen, but with 15·96 parts, and therefore we shall obtain, taking H = 1, not the above-cited figures, but for silver 107·68, for bromine 79·75, for iodine 126·53, magnitudes which are still further removed from whole numbers. Besides which, if Marignac's proposition were true the combining weight of silver determined by one method—*e.g.* by the analysis of silver chlorate combined with the synthesis of silver chloride—would not agree well with the combining weight determined by another method —*e.g.* by means of the analysis of silver iodate and the synthesis of silver iodide. If in one case a basic salt could be obtained, in the other case an acid salt might be obtained. Then the analysis of the acid salt would give different results from that of the basic salt. Thus Marignac's arguments cannot serve as a support for the vindication of Proust's hypothesis.

In conclusion, I think it will not be out of place to cite the following passage from a paper read by me before the London Chemical Society in 1889 (Appendix II.), where I touch on the hypothesis of the complexity of the elements recognised in chemistry, owing to the fact that many have endeavoured to apply the periodic law to the justification of this idea 'taken from a remote antiquity, when it was found convenient to admit the existence of many gods and of a unique matter.'

'When we try to explain the origin of the idea of a unique primary matter, we easily trace that, in the absence of deductions from experiment, it derives its origin from the scientifically philosophical attempt at discovering some kind of unity in the immense diversity of individualities which we see around. In classical times such a tendency could only be satisfied by conceptions about the immaterial world. As to the material world, our ancestors were compelled to resort to some hypothesis, and they adopted the idea of unity in the formative material, because they were not able to evolve the conception of any other possible unity in order to connect the multifarious relations of matter. Responding to the same legitimate scientific tendency, natural science has discovered throughout the universe a unity of plan, a unity of forces, and a unity of matter; and the convincing conclusions of modern science compel every one to admit these kinds of unity. But while we admit unity in many things, we none the less must also explain the individuality and the apparent diversity which we cannot fail to trace everywhere.

heavy platinum metals, osmium, iridium, and platinum, as copper and silver do to the two preceding series. The atomic weight of gold is nearly equal to their atomic weights ;[28] it is also dense like these metals. It also gives various grades of oxidation, which are also feeble, both in a basic and an acid sense. Whilst near to osmium, iridium, and platinum, gold at the same time is able, like copper and silver, to form compounds which answer to the type RX—that is, oxides of the composition R_2O. Cuprous chloride, CuCl, silver chloride, AgCl, and aurous chloride, AuCl, are substances which are very much alike in their physical and chemical properties. They are insoluble in water, but dissolve in hydrochloric acid and ammonia, in potassium cyanide, sodium thiosulphate, &c. Just as copper forms a link between the iron metals and zinc, and as silver unites the light platinum metals with cadmium, so also gold presents a transition from the heavy platinum metals to mercury. Copper gives saline compounds of the types CuX and CuX_2, silver of the type AgX, whilst gold, besides compounds of the type AuX, very easily and most frequently forms AuX_3. The compounds

It was said of old "Give us a fulcrum and it will become easy to displace the earth." So also we must say, "Give anything that is individualised, and the apparent diversity will be easily understood." Otherwise, how could unity result in a multitude?

'After a long and painstaking research, natural science has discovered the individualities of the chemical elements, and therefore it is now capable, not only of analysing, but also of synthetising; it can understand and grasp the general and unity, as well as the individualised and multitudinous. Unity and the general, like time and space, like force and motion, vary uniformly. The uniform admit of interpolations, revealing every intermediate phase; but the multitudinous, the individualised—like ourselves, like the chemical elements, like the members of a peculiar periodic function of elements, like Dalton's multiple proportions—is characterised in another way. We see in it—side by side with a general connecting principle—leaps, breaks of continuity, points which escape from the analysis of the infinitely small—a complete absence of intermediate links. Chemistry has found an answer to the question as to the causes of multitudes, and while retaining the conception of many elements, all submitted to the discipline of a general law, it offers an escape from the Indian Nirvana—the absorption in the universal—replacing it by the individualised. However, the place for individuality is so limited by the all-grasping, all-powerful universal, that it is merely a fulcrum for the understanding of multitude in unity.'

[28] One would expect from the periodic law and analogies with the series iron, cobalt, nickel, copper, zinc, that the atomic weights of the elements of the series osmium, iridium, platinum, gold, mercury, would rise in this order, and at the time of the establishment (1869) of the periodic law, the determinations of Berzelius, Rose, and others gave the following values for the atomic weights: Os = 200, I = 197, Pt = 198, Au = 196, Hg = 200. The fulfilment of the expectations of the periodic law was given in the first place by the fresh determinations (Seubert, Dittmar, and Arthur) of the atomic weight of platinum, which proved to be nearly 196, if O = 16 (as Marignac, Brauner, and others propose); in the second place, by the fact that Seubert proved that the atomic weight of osmium is really less than that of platinum, and approximately Os = 191; and, in the third place, by the fact that after the researches of Krüss, Thorpe, and Laurie there was no doubt that the atomic weight of gold is greater than that of platinum—namely, nearly 197.

of this type frequently pass into those of the lower type, just as PtX_4 passes into PtX_2 and the same is observable in the elements which, in their atomic weights, follow gold. Mercury gives HgX_2 and HgX. Thallium gives TlX_3 and TlX, lead gives PbX_4 and PbX_2. On the other hand, gold in a qualitative respect differs from silver and copper in the *extreme ease* with which all its compounds are *reduced to metal* by many means. This is not only accomplished by many reducing agents, but also by the action of heat. Thus its chlorides and oxides lose their chlorine and oxygen when heated, and, if the temperature be sufficiently high, these elements are entirely expelled and metallic gold alone remains. Its compounds, therefore, act as oxidising agents.[29]

In nature gold occurs in the primary and chiefly in quartzose rocks, and especially in quartz veins, as in the Urals (at Berezoffsk), in Australia, and in California. The native gold is extracted from these rocks by subjecting them to a mechanical treatment consisting of crushing and washing. Therefore poor ores are seldom treated, all the more as in many localities nature has already accomplished a similar disintegration of the hard rocky matter containing gold.[30] These disintegrated rocks, washed by rain and other water, have formed gold-bearing deposits, which are known as *alluvial gold deposits*. Gold-bearing soil is sometimes met with on the surface and sometimes under the upper soil, but more frequently along the banks of dried-up water-

[29] Heavy atoms, although they may present many points of analogy with lighter atoms, are more easily isolated; thus $C_{16}H_{32}$, although it combines with Br_2 like C_2H_4, and although it has the same common properties, yet reacts with much greater difficulty than C_2H_4; the heavy atoms and molecules are, so to say, inert, and already saturated by themselves. Gold in its higher grade of oxidation, Au_2O_3, presents feeble basic properties and weakly-developed acid properties, so that this oxide of gold, Au_2O_3, may be referred to the class of feeble acid oxides, like platinic oxide. This is not the case in the highest known oxides of copper and silver. But in the lower grade of oxidation, aurous oxide, Au_2O, gold, like silver and copper, presents basic properties, although they are unenergetic. In this respect it stands very close in its properties, although not in its types of combination (AuX and AuX_3), to platinum (PtX_2 and PtX_4) and its analogues.

As yet the general chemical characteristics of gold and its compounds have not been fully investigated. This is partly due to very few having undertaken researches on the compounds of this metal, owing to its difficult accessibility for working in large quantities. As the atomic weight of gold is high (Au = 197), the preparation of its compounds requires that it should be taken in large quantities, which forms an obstacle to its being fully studied. Therefore, the facts concerning the history of this metal are rarely distinguished by that exactitude with which many facts have been established concerning other elements more accessible, and long known in use.

[30] However, in recent times, especially since about 1870, since chlorine (either as a solution of the gas or as bleaching powder) and bromine have been applied to the extraction of finely-divided gold from poor ores (previously roasted in order to drive off arsenic, sulphur, and oxidise the iron, Fe), the extraction of gold from quartz, and of that which is held in pyrites, increases from year to year, and begins to equal the amount extracted from alluvial deposits.

courses and running streams. The sand of many rivers contains, however, a very small amount of gold, which it is not profitable to work; for example, that of the Alpine rivers contains 5 parts of gold in 10,000,000 parts of sand. The richest gold deposits are those of Siberia, especially in the southern parts of the Government of Yeniseisk, the South Urals, Mexico, California, and the southern coast of Australia, and then the comparatively poorer alluvial deposits of many countries (Hungary, the Alps, and Spain in Europe). The extraction of the gold from alluvial deposits is based on the principle of levigation; the earth is washed, while constantly agitated, by a stream of water, which carries away the lighter portion of the earth, and leaves the coarser particles of the rock and heavier particles of the gold, together with certain substances which accompany it, in the washing apparatus. The extraction of this *washed* gold only necessitates mechanical appliances,[31] and it is not therefore surprising that gold was known to savages and in the most remote period of history. It sometimes occurs in crystals belonging to the regular system, but in the majority of cases in nuggets or grains of greater or less magnitude. It always contains silver (from very small quantities up to 30 p.c., when it is called 'electrum') and certain other metals, among which lead and rhodium are sometimes found.

The separation of the silver from gold is generally carried on with

[31] But the particles of gold are sometimes so small that a large amount is lost during the washing. It is then profitable to have recourse to the extraction by chlorine and bromine (Note 30).

In speaking of the extraction of gold the following remarks may not be out of place.

In California advantage is taken of water supplied from high altitudes in order to have a powerful head of water, with which the rocks are directly washed away, thus avoiding the greater portion of the mechanical labour required for the exploitation of these deposits.

The last residues of gold are sometimes extracted from sand by washing them with mercury, which dissolves the gold. The sand mixed with water is caused to come into contact with mercury during the washing. The mercury is then distilled.

Many sulphurous ores, even pyrites, contain a small amount of gold. Compounds of gold with bismuth, $BiAu_2$, tellurium, $AuTe_2$ (calverite), &c., have been found, although rarely.

Among the minerals which accompany gold, and from which the presence of gold may be expected, we may mention white quartz, titanic and magnetic iron ores, and also the following, which are of rarer occurrence, zircon, topaz, garnet, and such like. The concentrated gold washings first undergo a mechanical treatment, and the impure gold then obtained is treated for pure gold by various methods. If the gold contain a considerable amount of foreign metals, especially lead and copper, it is sometimes cupelled, like silver, so that the oxidisable metals may be absorbed by the cupel in the form of oxides, but in every case the gold is obtained together with silver, because the latter metal also is not oxidised. Sometimes the gold is extracted by means of mercury (and the mercury subsequently driven off by distillation), that is, by amalgamation, or by smelting it with lead (which is afterwards removed by oxidation) and processes like those employed for the extraction of silver, because gold, like silver, does not oxidise, is dissolved by lead and mercury, and is non-volatile.

great precision, as the presence of the silver in the gold does not increase its value for exchange, and it can be substituted by other less valuable metals, so that it is an entire gain to extract the silver, as a precious metal, from its alloy with gold. This separation is conducted by different methods. Sometimes the argentiferous gold is melted in crucibles, together with a mixture of common salt and powdered bricks. The greater portion of the silver is thus converted into the chloride, which fuses and is absorbed by the slags, from which it may be extracted by the usual methods. The silver is also extracted from gold by treating it with boiling sulphuric acid, which does not act on the gold but dissolves the silver. But if the alloy does not contain a large proportion of silver it cannot be extracted by this method, or, at all events, the separation will be imperfect, and therefore a fresh amount of silver is added (by fusion) to the gold, in such a quantity that the alloy contains twice as much silver as gold. The silver which is added is, preferably such as contains gold, which is very frequently the case. The alloy thus formed is poured in a thin stream into water, by which means it is obtained in a granulated form, which is then boiled with strong sulphuric acid, three parts of acid being used for one part of alloy. The sulphuric acid extracts all the silver without acting on the gold. It is best, however, to pour off the first portion of the acid, which has dissolved the silver, and then treat the residue of still imperfectly pure gold with a fresh quantity of sulphuric acid. The gold is thus obtained in the form of powder, which is washed with water until it is quite free from silver. The silver is precipitated from the solution by means of copper, so that cupric sulphate and metallic silver are obtained. This process is carried out in many countries, as in Russia, at the Government mints.

Gold is generally used in practice alloyed with copper; because pure gold, like pure silver, is very soft, and therefore soon worn away. In assaying or determining the amount of pure gold in such an alloy it is usual to add silver to the gold in order to make up an alloy containing three parts of silver to one of gold. This is known as quartation (because the alloy contains $\frac{1}{4}$ of gold), and the resultant alloy is treated with nitric acid. If the silver be not in excess over the gold, it is not all dissolved by the nitric acid, and this is the reason of the quartation. The amount of pure gold (assay) is determined by weighing the gold which remains after this treatment. English gold (=22 carats) coinage is composed of an alloy containing 91·66 p.c. of gold, but for many articles gold is frequently used containing a larger amount of foreign metals.

Pure gold may be obtained from gold alloys by dissolving in aqua

regia, and then adding ferrous sulphate to the solution or heating it with a solution of oxalic acid. These deoxidising agents reduce the gold, but not the other metals. The chlorine combined with the gold then acts like free chlorine. The gold, thus reduced, is precipitated as an exceedingly fine brown powder. It is then washed with water, and fused with nitre or borax. Pure gold reflects a yellow light, and in the form of very thin sheets, into which it can be hammered and rolled, it transmits a bluish-green light. The specific gravity of gold is nearly 19·5. It fuses at 1090°—at a higher temperature than silver—and can be drawn into exceedingly fine wires and thin sheets. Gold leaf is used for gilding—for instance, it is glued on to wood by means of drying oils. With its softness and ductility, gold is distinguished for its tenacity, and a gold wire two millimetres thick breaks under a load of 68 kilograms. Gold vaporises even at a furnace heat, so that it imparts a greenish colour to a flame passing over it in a furnace. In a chemical respect, gold presents, as is already seen from its general characteristics given above, an example of the so-called noble metals—*i.e.*, it is incapable of being oxidised under any heat, and its oxide is decomposed when calcined. Only chlorine and bromine combine directly with it at the ordinary temperature, but many other metals and non-metals combine with it at a red heat—for example, sulphur, phosphorus, and arsenic. Mercury dissolves it with great ease. It dissolves in potassium cyanide in the presence of air; a mixture of sulphuric acid with nitric acid dissolves it with the aid of heat, although in small quantity. It is also soluble in aqua regia and in selenic acid. Sulphuric, hydrochloric, nitric, and hydrofluoric acids and the caustic alkalis do not act on gold, but a mixture of hydrochloric acid with such oxidising agents as evolve chlorine naturally dissolves it like aqua regia.

As regards the compounds of gold, they belong, as was said above, to the types AuX_3 and AuX. *Auric chloride* or *gold trichloride*, $AuCl_3$, which is formed when gold is dissolved in aqua regia, belongs to the former and higher of these types. The solution of this substance in water has a yellow colour, and it may be obtained pure by evaporating the solution in aqua regia to dryness, but not to the point of decomposition. If the evaparation proceed to the point of crystallisation, a compound of gold chloride, and hydrochloric acid, $AuHCl_4$, is obtained, like the kindred compounds of platinum; but it easily parts with the acid and leaves auric chloride, which fuses into a red-brown liquid, and then solidifies into a crystalline mass. If dry chlorine be passed over gold in powder it forms a mixture of aurous and auric chlorides, but the aurous chloride is also decomposed by water into

gold and auric chloride. Auric chloride crystallises from its solutions as $AuCl_3,2H_2O$, which easily loses water, and the dry chloride loses two-thirds of its chlorine at 185°, forming aurous chloride, whilst at above 300° the latter chloride also loses its chlorine and leaves metallic gold. Auric chloride is the usual form in which gold occurs in solutions, and in which its salts are used in practice and for chemical purposes. It is soluble in water, alcohol, and ether. Light has a reducing action on these solutions, and after a time metallic gold is deposited upon the sides of vessels containing the solution. Hydrogen, at the moment of its evolution and even in a gaseous form, reduces gold from this solution to a metallic state. The reduction is more conveniently and usually accomplished by ferrous sulphate, and, in general, by the action of ferrous salts.[32]

If a solution of potassium hydroxide is added to a solution of auric chloride, a precipitate is first formed, which re-dissolves in an excess of the alkali. On being evaporated under the receiver of an air-pump, this solution yields yellow crystals, which present the same composition as the double salts $AuMCl_4$, with the substitution of the chlorine by oxygen—that is to say, *potassium aurate*, $AuKO_2$, is formed in crystals containing $3H_2O$. The solution has a distinctly alkaline reaction. *Auric oxide*, Au_2O_3, separates when this alkaline solution is boiled with an excess of sulphuric acid. But it then still retains some alkali; however, it may be obtained in a pure state as a brown powder by dissolving in nitric acid and diluting with water. The brown powder decomposes below 250° into gold and oxygen. It is insoluble in water and in many acids, but it dissolves in alkalis, which shows the acid character of this oxide. A hydroxide, $Au(OH)_3$, may be obtained as a brown powder by adding magnesium oxide to a solution of auric chloride and treating the resultant precipitate of magnesium aurate with

[32] Stannous chloride as a reducing agent also acts on auric chloride, and gives a red precipitate known as *purple of Cassius*. This substance, which probably contains a mixture or compound of aurous oxide and tin oxide, is used as a red pigment for china and glass. Oxalic acid, when heated, reduces metallic gold from its salts, which may be taken advantage of for separating it from its solutions. The oxidation which then takes place in the presence of water, may be expressed by the following equation: $2AuCl_3 + 3C_2H_2O_4 = 2Au + 6HCl + 6CO_2$. Nearly all organic substances have a reducing action on gold, and solutions of gold leave a violet stain on the skin.

Auric chloride, like platinic chloride, is distinguished for its clearly-developed faculty of forming double salts. These double salts, as a rule, belong to the type $AuMCl_4$. The above-mentioned compound of auric chloride with hydrochloric acid evidently belongs to the same type. The compounds $2KAuCl_4,5H_2O$, $NaAuCl_4,2H_2O$, $AuNH_4Cl_4,H_2O$, $Mg(AuCl_4)_2,2H_2O$, and the like are easily crystallised in well-formed crystals. Auric bromide, $AuBr_3$, is extremely like the chloride. Auric cyanide is obtained easily in the form of a double salt of potassium, $KAu(CN)_4$, by mixing saturated and hot solutions of potassium cyanide with auric chloride and then cooling.

nitric acid. This hydroxide loses water at 100°, and gives auric oxide.[33]

The starting-point of the compounds of the type AuX is *gold monochloride* or *aurous chloride*, AuCl, which is formed, as mentioned above, by heating auric chloride at 185°. Aurous chloride forms a yellowish white powder; this, when heated with water, is decomposed into metallic gold and auric chloride, which passes into solution: $3AuCl = AuCl_3 + 2Au$. This decomposition is accelerated by the action of light. Hence it is obvious that the compounds corresponding with aurous oxide are comparatively unstable. But this only refers to the simple compounds AuX;[34] some of the complex compounds, on the contrary, form the most stable compounds of gold. Such, for example, is the cyanide of gold and potassium, $AuK(CN)_2$. It is formed, for instance, when gold dissolves in the presence of air in a solution of potassium cyanide: $4KCN + 2Au + H_2O + O = 2KAu(CN)_2 + 2KHO$. The same compound is formed in solution when many compounds of

[33] If ammonia is added to a solution of auric chloride, it forms a yellow precipitate of the so-called fulminating gold, which contains gold, chlorine, hydrogen, nitrogen, and oxygen, but its formula is not known with certainty. It is probably a sort of ammonio-metallic compound, $Au_2O_3,4NH_3$, or amide (like the mercury compound). This precipitate explodes at 140°, but when left in the presence of solutions containing ammonia it loses all its chlorine and becomes unexplosive. In this form the composition $Au_2O_3,2NH_3,H_2O$ is ascribed to it, but this is uncertain. Auric sulphide, Au_2S_3, is obtained by the action of hydrogen sulphide on a solution of auric chloride, and also by directly fusing sulphur with gold. It has an acid character, and therefore dissolves in sodium and ammonium sulphides.

[34] Potassium aurous cyanide corresponds with the salts of the type $AuKX_2$, like PtK_2X_4, with which we became acquainted in the last chapter. We will enumerate several of the representatives of this class of compounds. If auric chloride, $AuCl_3$, be mixed with a solution of sodium thiosulphate, then the gold passes into a colourless solution, which deposits colourless crystals, containing a double thiosulphate of gold and sodium, which are easily soluble in water but are precipitated by alcohol. The composition of this salt is $Na_3Au(S_2O_3)_2,2H_2O$. If the sodium thiosulphate be represented as NaS_2O_3Na, then the double salt in question will be $AuNa(S_2O_3Na)_2,2H_2O$, according to the type $AuNaX_2$. The solution of this colourless and easily crystallisable salt has a sweet taste, and the gold is not separated from it either by ferrous sulphate or oxalic acid. This salt, which is known as *Fordos and Giles's salt*, is used in medicine and photography. In general, aurous oxide exhibits a distinct inclination to the formation of similar double salts, as we saw also with PtX_2; for example, it forms similar salts with sulphurous acid. Thus if a solution of sodium sulphite be gradually added to a solution of oxide of gold in sodium hydroxide, then the precipitate at first formed redissolves to a colourless solution, which contains the double salt $Na_3Au(SO_3)_2 = AuNa(SO_3Na)_2$. The solution of this salt, when mixed with barium chloride, first forms a precipitate of barium sulphite, and then a red barium double salt, which corresponds with the above sodium salt.

The oxygen compound of the type AuX, *aurous oxide*, Au_2O, is obtained as a greenish violet powder on mixing aurous chloride with potassium chloride in the cold. With hydrochloric acid this oxide gives gold and auric chloride, and when heated it easily splits up into oxygen and metallic gold.

gold are mixed with potassium cyanide, because if a higher compound of gold be taken, it is reduced by the potassium cyanide into aurous oxide, which dissolves in potassium cyanide and forms $KAu(CN)_2$. This substance is soluble in water, and gives a colourless solution, which can be kept for a long time and is employed in electro-gilding—that is, for coating other metallic objects with a layer of gold, which is deposited if the object be connected with the negative pole of a battery and a gold plate be placed on the positive pole and an electrical current passed between them. Then the gold which is situated on the positive pole will dissolve, whilst a coating of gold from the solution will be deposited on the object.

APPENDIX I.

AN ATTEMPT TO APPLY TO CHEMISTRY ONE OF THE PRINCIPLES OF NEWTON'S NATURAL PHILOSOPHY.

BY PROFESSOR MENDELÉEFF.

A LECTURE DELIVERED AT THE ROYAL INSTITUTION OF GREAT BRITAIN ON FRIDAY, MAY 31, 1889.

NATURE, inert to the eyes of the ancients, has been revealed to us as full of life and activity. The conviction that motion pervaded all things, which was first realised with respect to the stellar universe, has now extended to the unseen world of atoms. No sooner had the human understanding denied to the earth a fixed position and launched it along its path in space, than it was sought to fix immovably the sun and the stars. But astronomy has demonstrated that the sun moves with unswerving regularity through the star-set universe at the rate of about 50 kilometres per second. Among the so-called fixed stars are now discerned manifold changes and various orders of movement. Light, heat, electricity—like sound—have been proved to be modes of motion; to the realisation of this fact modern science is indebted for powers which have been used with such brilliant success, and which have been expounded so clearly at this lecture table by Faraday and by his successors. As, in the imagination of Dante, the invisible air became peopled with spiritual beings, so before the eyes of earnest investigators, and especially before those of Clerk Maxwell, the invisible mass of gases became peopled with particles: their rapid movements, their collisions, and impacts became so manifest that it seemed almost possible to count the impacts and determine many of the peculiarities or laws of their collisions. The fact of the existence of these invisible motions may at once be made apparent by demonstrating the difference in the rate of diffusion through porous bodies of the light and rapidly moving atoms of hydrogen and the heavier and more sluggish particles of air. Within the masses of liquid and of solid bodies we have been forced to acknowledge the existence of persistent though limited motion of their ultimate particles, for otherwise it would be impossible to explain, for example, the celebrated experiments of Graham on diffusion through liquid and colloidal substances. If there were, in our times, no belief in the mole-

cular motion in solid bodies, could the famous Spring have hoped to attain any result by mixing carefully-dried powders of potash saltpetre and sodium acetate, in order to produce, by pressure, a chemical reaction between these substances through the interchange of their metals, and have derived, for the conviction of the incredulous, a mixture of two hygroscopic though solid salts—sodium nitrate and potassium acetate?

In these invisible and apparently chaotic movements, reaching from the stars to the minutest atoms, there reigns, however, a harmonious order which is commonly mistaken for complete rest, but which is really a consequence of the conservation of that dynamic equilibrium which was first discerned by the genius of Newton, and which has been traced by his successors in the detailed analysis of the particular consequences of the great generalisation, namely, relative immovability in the midst of universal and active movement.

But the unseen world of chemical changes is closely analogous to the visible world of the heavenly bodies, since our atoms form distinct portions of an invisible world, as planets, satellites, and comets form distinct portions of the astronomer's universe; our atoms may therefore be compared to the solar systems, or to the systems of double or of single stars: for example, ammonia (NH_3) may be represented in the simplest manner by supposing the sun, nitrogen, surrounded by its planets of hydrogen; and common salt (NaCl) may be looked on as a double star formed of sodium and chlorine. Besides, now that the indestructibility of the elements has been acknowledged, chemical changes cannot otherwise be explained than as changes of motion, and the production by chemical reactions of galvanic currents, of light, of heat, of pressure, or of steam power, demonstrate visibly that the processes of chemical reaction are inevitably connected with enormous though unseen displacements, originating in the movements of atoms in molecules. Astronomers and natural philosophers, in studying the visible motions of the heavenly bodies and of matter on the earth, have understood and have estimated the value of this store of energy. But the chemist has had to pursue a contrary course. Observing in the physical and mechanical phenomena which accompany chemical reactions the quantity of energy manifested by the atoms and molecules, he is constrained to acknowledge that within the molecules there exist atoms in motion, endowed with an energy which, like matter itself, is neither being created nor capable of being destroyed. Therefore, in chemistry, we must seek dynamic equilibrium not only between the molecules, but also in their midst among their component atoms. Many conditions of such equilibrium have been determined, but much remains to be done, and it is not uncommon, even in these days, to find that some chemists forget that there is the possibility of motion in the interior of molecules, and therefore represent them as being in a condition of death-like inactivity.

Chemical combinations take place with so much ease and rapidity, possess so many special characteristics, and are so numerous, that their simplicity and order was for a long time hidden from investigators. Sympathy, relationship, all the caprices or all the fancifulness of human intercourse, seemed to have found complete analogies in chemical combinations, but with this difference, that the characteristics of the material substances—such as silver, for example, or of any other body—remain unchanged in every sub-

division from the largest masses to the smallest particles, and consequently their characteristics must be a property of its particles. But the world of heavenly luminaries appeared equally fanciful at man's first acquaintance with it, so much so, that the astrologers imagined a connection between the individualites of men and the conjunctions of planets. Thanks to the genius of Lavoisier and of Dalton, man has been able, in the unseen world of chemical combinations, to recognise laws of the same simple order as those which Copernicus and Kepler proved to exist in the planetary universe. Man discovered, and continues every hour to discover, *what* remains unchanged in chemical evolution, and *how* changes take place in combinations of the unchangeable. He has learned to predict, not only what possible combinations may take place, but also the very existence of atoms of unknown elementary substances, and has besides succeeded in making innumerable practical applications of his knowledge to the great advantage of his race, and has accomplished this notwithstanding that notions of sympathy and affinity still preserve a strong vitality in science. At present we cannot apply Newton's principles to chemistry, because the soil is only being now prepared. The invisible world of chemical atoms is still waiting for the creator of chemical mechanics. For him our age is collecting a mass of materials, the inductions of well-digested facts, and many-sided inferences similar to those which existed for Astronomy and Mechanics in the days of Newton. It is well also to remember that Newton devoted much time to chemical experiments, and while considering questions of celestial mechanics, persistently kept in view the mutual action of those infinitely small worlds which are concerned in chemical evolutions. For this reason, and also to maintain the unity of laws, it seems to me that we must, in the first instance, seek to harmonise the various phases of contemporary chemical theories with the immortal principles of the Newtonian natural philosophy, and so hasten the advent of true chemical mechanics. Let the above considerations serve as my justification for the attempt which I propose to make to act as a champion of the universality of the Newtonian principles, which I believe are competent to embrace every phenomenon in the universe, from the rotation of the fixed stars to the interchanges of chemical atoms.

In the first place I consider it indispensable to bear in mind that, up to quite recent times, only a one-sided affinity has been recognised in chemical reactions. Thus, for example, from the circumstance that red-hot iron decomposes water with the evolution of hydrogen, it was concluded that oxygen had a greater affinity for iron than for hydrogen. But hydrogen, in presence of red-hot iron scale, appropriates its oxygen and forms water, whence an exactly opposite conclusion may be formed.

During the last ten years a gradual, scarcely perceptible, but most important change has taken place in the views, and consequently in the researches, of chemists. They have sought everywhere, and have always found, systems of conservation or dynamic equilibrium substantially similar to those which natural philosophers have long since discovered in the visible world, and in virtue of which the position of the heavenly bodies in the universe is determined. There where one-sided affinities only were at first detected, not only secondary or lateral ones have been found, but even those.

which are diametrically opposite; yet among these, dynamical equilibrium establishes itself not by excluding one or other of the forces, but regulating them all. So the chemist finds in the flame of the blast furnace, in the formation of every salt, and, with especial clearness, in double salts and in the crystallisation of solutions, not a fight ending in the victory of one side, as used to be supposed, but the conjunction of forces; the peace of dynamic equilibrium resulting from the action of many forces and affinities. Carbonaceous matters, for example, burn at the expense of the oxygen of the air, yielding a quantity of heat, and forming products of combustion, in which it was thought that the affinities of the oxygen with the combustible elements were satisfied. But it appeared that the heat of combustion was competent to decompose these products, to dissociate the oxygen from the combustible elements, and therefore to explain combustion fully it is necessary to take into account the equilibrium between opposite reactions, between those which evolve and those which absorb heat.

In the same way, in the case of the solution of common salt in water, it is necessary to take into account, on the one hand, the formation of compound particles generated by the combination of salt with water, and, on the other, the disintegration or scattering of the new particles formed, as well as of those originally contained. At present we find two currents of thought, apparently antagonistic to each other, dominating the study of solutions: according to the one, solution seems a mere act of building up or association; according to the other, it is only dissociation or disintegration. The truth lies, evidently, between these views; it lies, as I have endeavoured to prove by my investigations into aqueous solutions, in the dynamic equilibrium of particles tending to combine and also to fall asunder. The large majority of chemical reactions which appeared to act victoriously along one line have been proved capable of acting as victoriously even along an exactly opposite line. Elements which utterly decline to combine directly may often be formed into comparatively stable compounds by indirect means, as, for example, in the case of chlorine and carbon; and consequently the sympathies and antipathies which it was thought to transfer from human relations to those of atoms should be laid aside until the mechanism of chemical relations is explained. Let us remember, however, that chlorine, which does not form with carbon the chloride of carbon, is strongly absorbed, or, as it were, dissolved by carbon, which leads us to suspect incipient chemical action even in an external and purely surface contact, and involuntarily gives rise to conceptions of that unity of the forces of nature which has been so energetically insisted on by Sir William Grove and formulated in his famous paradox. Grove noticed that platinum, when fused in the oxyhydrogen flame, during which operation water is formed, when allowed to drop into water decomposes the latter and produces the explosive oxyhydrogen mixture. The explanation of this paradox, as of many others which arose during the period of chemical renaissance, has led, in our time, to the promulgation by Henri Sainte-Claire Deville of the conception of dissociation and of equilibrium, and has recalled the teaching of Berthollet, which, notwithstanding its brilliant confirmation by Heinrich Rose and Dr. Gladstone, had not, up to that period, been included in received chemical views.

Chemical equilibrium in general, and dissociation in particular, are now being so fully worked out in detail, and applied in such various ways, that I do not allude to them to develop, but only use them as examples by which to indicate the correctness of a tendency to regard chemical combinations from points of view differing from those expressed by the term hitherto appropriated to define chemical forces, namely, 'affinity.' Chemical equilibria, dissociation, the speed of chemical reactions, thermochemistry, spectroscopy, and, more than all, the determination of the influence of masses and the search for a connection between the properties and weights of atoms and molecules—in one word, the vast mass of the most important chemical researches of the present day—clearly indicates the near approach of the time when chemical doctrines will submit fully and completely to the doctrine which was first announced in the Principia of Newton.

In order that the application of these principles may bear fruit it is evidently insufficient to assume that statical equilibrium reigns alone in chemical systems or chemical molecules: it is necessary to grasp the conditions of possible states of dynamical equilibria, and to apply to them kinetic principles. Numerous considerations compel us to renounce the idea of statical equilibrium in molecules, and the recent yet strongly-supported appeals to dynamic principles constitute, in my opinion, the foundation of the modern teaching relating to atomicity, or the valency of the elements, which usually forms the basis of investigations into organic or carbon compounds.

This teaching has led to brilliant explanations of very many chemical relations and to cases of isomerism, or the difference in the properties of substances having the same composition. It has been so fruitful in its many applications and in the foreshadowing of remote consequences, especially respecting carbon compounds, that it is impossible to deny its claims to be ranked as a great achievement of chemical science. Its practical application to the synthesis of many substances of the most complicated composition entering into the structure of organised bodies, and to the creation of an unlimited number of carbon compounds, among which the colours derived from coal tar stand prominently forward, surpass the synthetical powers of Nature itself. Yet this teaching, as applied to the structure of carbon compounds, is not on the face of it directly applicable to the investigation of other elements, because in examining the first it is possible to assume that the atoms of carbon have always a definite and equal number of affinities, whilst in the combinations of other elements this is evidently inadmissible. Thus, for example, an atom of carbon yields only one compound with four atoms of hydrogen and one with four atoms of chlorine in the molecule, whilst the atoms of chlorine and hydrogen unite only in the proportions of one to one. Simplicity is here evident, and forms a point of departure from which it is easy to move forward with firm and secure tread. Other elements are of a different nature. Phosphorus unites with three and with five atoms of chlorine, and consequently the simplicity and sharpness of the application of structural conceptions are lost. Sulphur unites only with two atoms of hydrogen, but with oxygen it enters into higher orders of combination. The periodic relationship which exists among all the properties of the elements—such, for example, as their ability to enter into various combinations—and

their atomic weights, indicate that this variation in atomicity is subject to one perfectly exact and general law, and it is only carbon and its near analogues which constitute cases of permanently preserved atomicity. It is impossible to recognise as constant and fundamental properties of atoms, powers which, in substance, have proved to be variable. But by abandoning the idea of permanence, and of the constant saturation of affinities—that is to say, by acknowledging the possibility of free affinities—many retain a comprehension of the atomicity of the elements 'under given conditions'; and on this frail foundation they build up structures composed of chemical molecules, evidently only because the conception of manifold affinities gives, at once, a simple statical method of estimating the composition of the most complicated molecules.

I shall enter neither into details, nor into the various consequences following from these views, nor into the disputes which have sprung up respecting them (and relating especially to the number of isomerides possible on the assumption of free affinities), because the foundation or origin of theories of this nature suffers from the radical defect of being in opposition to dynamics. The molecule, as even Laurent expressed himself, is represented as an architectural structure, the style of which is determined by the fundamental arrangement of a few atoms, whilst the decorative details, which are capable of being varied by the same forces, are formed by the elements entering into the combination. It is on this account that the term 'structural' is so appropriate to the contemporary views of the above order, and that the 'structuralists' seek to justify the tetrahedric, plane, or prismatic disposition of the atoms of carbon in benzene. It is evident that the consideration relates to the statical position of atoms and molecules and not to their kinetic relations. The atoms of the structural type are like the lifeless pieces on a chess board: they are endowed but with the voices of living beings, and are not those living beings themselves; acting, indeed, according to laws, yet each possessed of a store of energy which, in the present state of our knowledge, must be taken into account.

In the days of Haüy, crystals were considered in the same statical and structural light, but modern crystallographers, having become more thoroughly acquainted with their physical properties and their actual formation, have abandoned the earlier views, and have made their doctrines dependent on dynamics.

The immediate object of this lecture is to show that, starting with Newton's third law of motion, it is possible to preserve to chemistry all the advantages arising from structural teaching, without being obliged to build up molecules in solid and motionless figures, or to ascribe to atoms definite limited valencies, directions of cohesion, or affinities. The wide extent of the subject obliges me to treat only a small portion of it, namely of *substitutions*, without specially considering combinations and decompositions, and even then limiting myself to the simplest examples, which, however, will throw open prospects embracing all the natural complexity of chemical relations. For this reason, if it should prove possible to form groups similar, for example, to H_4 or CH_6 as the remnants of molecules CH_4 or C_2H_7 we shall not pause to consider them, because, as far as we know, they fall asunder into

two parts, $H_2 + H_2$ or $CH_4 + H_2$, as soon as they are even temporarily formed, and are capable of separate existence, and therefore can take no part in the elementary act of substitution. With respect to the simplest molecules which we shall select—that is to say, those of which the parts have no separate existence, and therefore cannot appear in substitutions—we shall consider them according to the periodic law, arranging them in direct dependence on the atomic weight of the elements.

Thus, for example, the molecules of the simplest hydrogen compounds—

HF	H_2O	H_3N	H_4C
hydrofluoric acid	water	ammonia	methane

correspond with elements the atomic weights of which decrease consecutively

$$F = 19, \qquad O = 16, \qquad N = 14, \qquad C = 12.$$

Neither the arithmetical order (1, 2, 3, 4 atoms of hydrogen) nor the total information we possess respecting the elements will permit us to interpolate into this typical series one more additional element; and therefore we have here, for hydrogen compounds, a natural base on which are built up those simple chemical combinations which we take as typical. But even they are competent to unite with each other, as we see, for instance, in the property which hydrofluoric acid has of forming a hydrate—that is, of combining with water; and the similar attribute of ammonia, resulting in the formation of a caustic alkali, NH_3,H_2O, or NH_4OH.

Having made these indispensable preliminary observations, I may now attack the problem itself and attempt to explain the so-called structure, or rather construction, of molecules—that is to say, their constitution and transformations—without having recourse to the teaching of 'structuralists,' but on Newton's dynamical principles.

Of Newton's three laws of motion, only the third can be applied directly to chemical molecules when regarded as systems of atoms among which it must be supposed that there exist common influences or forces, and resulting compounded relative motions. Chemical reactions of every kind are undoubtedly accomplished by changes in these internal movements, respecting the nature of which nothing is known at present, but the existence of which the mass of evidence collected in modern times forces us to acknowledge as forming part of the common motion of the universe, and as a fact further established by the circumstance that chemical reactions are always characterised by changes of volume or the relations between the atoms or the molecules. Newton's third law, which is applicable to every system, declares that, 'action is always associated with reaction, and is equal to it.' The brevity and conciseness of this axiom was, however, qualified by Newton in a more expanded statement, 'the action of bodies one upon another are always equal, and in opposite directions.' This simple fact constitutes the point of departure for explaining dynamic equilibrium—that is to say, systems of conservancy. It is capable of satisfying even the dualists, and of explaining, without additional assumptions, the preservation of those chemical types which Dumas, Laurent, and Gerhardt created unit types, and those views of atomic combinations which the structuralists express by atomicity or the

valency of the elements, and, in connection with them, the various numbers of affinities. In reality, if a system of atoms or a molecule be given, then in it, according to the third law of Newton, each portion of atoms acts on the remaining portion in the same manner, and with the same force as the second set of atoms acts on the first. We infer directly from this consideration that both sets of atoms, forming a molecule, are not only equivalent with regard to themselves, as they must be according to Dalton's law, but also that they may, if united, replace each other. Let there be a molecule containing atoms A B C, it is clear that, according to Newton's law, the action of A on B C must be equal to the action of B C on A, and if the first action is directed on B C, then the second must be directed on A, and consequently then, where A can exist in dynamic equilibrium, B C may take its place and act in a like manner. In the same way the action of C is equal to the action of A B. In one word every two sets of atoms forming a molecule are equivalent to each other, and may take each other's place in other molecules, or, having the power of balancing each other, the atoms or their complements are endowed with the power of replacing each other. Let us call this consequence of an evident axiom 'the principle of substitution,' and let us apply it to those typical forms of hydrogen compounds which we have already discussed, and which, on account of their simplicity and regularity, have served as starting-points of chemical argument long before the appearance of the doctrine of structure.

In the type of hydrofluoric acid, HF, or in systems of double stars, are included a multitude of the simplest molecules. It will be sufficient for our purpose to recall a few: for example, the molecules of chlorine, Cl_2, and of hydrogen, H_2, and hydrochloric acid, HCl, which is familiar to all in aqueous solution as spirits of salt, and which has many points of resemblance with HF, HBr, HI. In these cases division into two parts can only be made in one way, and therefore the principle of substitution renders it probable that exchanges between the chlorine and the hydrogen can take place, if they are competent to unite with each other. There was a time when no chemist would even admit the idea of any such action; it was then thought that the power of combination indicated a polar difference of the molecules in combination, and this thought set aside all idea of the substitution of one component element by another.

Thanks to the observations and experiments of Dumas and Laurent fifty years ago, such fallacies were dispelled, and in this manner, the principle of substitution was exhibited. Chlorine and bromine acting on many hydrogen compounds, occupy immediately the place of their hydrogen, and the displaced hydrogen, with another atom of chlorine or bromine, forms hydrochloric acid or bromide of hydrogen. This takes place in all typical hydrogen compounds. Thus chlorine acts on this principle on gaseous hydrogen—reaction, under the influence of light, resulting in the formation of hydrochloric acid. Chlorine acting on the alkalis, constituted similarly to water, and even on water itself—only, however, under the influence of light and only partially because of the instability of HClO—forms by this principle bleaching salts, which are the same as the alkalis, but with their hydrogen replaced by chlorine. In ammonia and in methane, chlorine can also replace the hydrogen. From ammonia is formed in this manner the so-called

chloride of nitrogen, NCl_3, which decomposes very readily with violent explosion on account of the evolved gases, and falls asunder as chlorine and nitrogen. Out of marsh gas, or methane, CH_4, may be obtained consecutively, by this method, every possible substitution, of which chloroform, $CHCl_3$, is the best known, and carbon tetrachloride, CCl_4, the most instructive. But by virtue of the fact that chlorine and bromine act, in the manner shown, on the simplest typical hydrogen compounds, their action on the more complicated ones may be assumed to be the same. This can be easily demonstrated. The hydrogen of benzene, C_6H_6, reacts feebly under the influence of light on liquid bromine, but Gustavson has shown that the addition of the smallest quantity of metallic aluminium causes energetic action and the evolution of large volumes of hydrogen bromide.

If we pass on to the second typical hydrogen compound—that is to say, water—its molecule, HOH, may be split up in two ways: either into an atom of hydrogen and a semimolecule of hydrogen peroxide, HO, or into oxygen, O, and two atoms of hydrogen, H; and therefore, according to the principle of substitution, it is evident that one atom of hydrogen can exchange with hydrogen oxide, HO, and two atoms of hydrogen, H, with one atom of oxygen, O.

Both these forms of substitution will constitute methods of oxidation—that is to say, of the entrance of oxygen into the compound—a reaction which is so common in nature as well as in the arts, taking place at the expense of the oxygen of the air or by the aid of various oxidising substances or bodies which part easily with their oxygen. There is no occasion to reckon up the unlimited number of cases of such oxidising reactions. It is sufficient to state that in the first of these oxygen is directly transferred, and the position, the chemical function, which hydrogen originally occupied is, after the substitution, occupied by the hydroxyl. Thus ammonia, NH_3, yields hydroxylamine, $NH_2(OH)$, a substance which retains many of the properties of ammonia.

Methane and a number of other hydrocarbons yield, by substitution of the hydrogen by its oxide, methyl alcohol, $CH_3(OH)$, and other alcohols. The substitution of one atom of oxygen for two atoms of hydrogen is equally common with hydrogen compounds. By this means alcoholic liquids containing ethyl alcohol, or spirits of wine, $C_2H_5(OH)$, are oxidised until they become vinegar or acetic acid, $C_2H_3O(OH)$. In the same way caustic ammonia, or the combination of ammonia with water, NH_3,H_2O, or $NH_4(OH)$, which contains a great deal of hydrogen, by oxidation exchanges four atoms of hydrogen for two atoms of oxygen, and becomes converted into nitric acid, $NO_2(OH)$. This process of conversion of ammonium salts into saltpetre goes on in the fields every summer, and with especial rapidity in tropical countries. The method by which this is accomplished, though complex, though involving the agency of all-permeating micro-organisms, is, in substance, the same as that by which alcohol is converted into acetic acid, or glycol, $C_2H_4(OH)_2$, into oxalic acid, if we view the process of oxidation in the light of the Newtonian principles.

But while speaking of the application of the principle of substitution to water, we need not multiply instances, but must turn our attention to two

special circumstances which are closely connected with the very mechanism of substitutions.

In the first place, the replacement of two atoms of hydrogen by one atom of oxygen may take place in two ways, because the hydrogen molecule is composed of two atoms, and therefore, under the influence of oxygen, the molecule forming water may separate before the oxygen has time to take its place. It is for this reason that we find, during the conversion of alcohol into acetic acid, that there is an interval during which is formed aldehyde, C_2H_4O, which, as its very name implies, is 'alcohol dehydrogenatum,' or alcohol deprived of hydrogen. Hence aldehyde combined with hydrogen yields alcohol; and united to oxygen, acetic acid.

For the same reason there should be, and there actually are, intermediate products between ammonia and nitric acid, $NO_2(HO)$, containing either less hydrogen than ammonia, less oxygen than nitric acid, or less water than caustic ammonia. Accordingly we find, among the products of the deoxidation of nitric acid and the oxidation of ammonia, not only hydroxylamine, but also nitrous oxide, nitrous and nitric anhydrides. Thus, the production of nitrous acid results from the removal of two atoms of hydrogen from caustic ammonia and the substitution of the oxygen for the hydrogen, $NO(OH)$; or by the substitution, in ammonia, of three atoms of hydrogen by hydroxyl, $N(OH)_3$, and by the removal of water: $N(OH)_3 - H_2O = NO(OH)$. The peculiarities and properties of nitrous acid—as, for instance, its action on ammonia and its conversion, by oxidation, into nitric acid—are thus clearly revealed.

On the other hand, in speaking of the principle of substitution as applied to water, it is necessary to observe that hydrogen and hydroxyl, H and OH, are not only competent to unite, but also to form combinations with themselves, and thus become H_2 and H_2O_2; and such are hydrogen and the peroxide thereof. In general, if a molecule AB exists, then molecules AA and BB can exist also. A direct reaction of this kind does not, however, take place in water, therefore undoubtedly, at the moment of formation, hydrogen reacts on hydrogen peroxide, as we can show at once by experiment; and further because hydrogen peroxide, H_2O_2, exhibits a structure containing a molecule of hydrogen, H_2, and one of oxygen, O_2, either of which is capable of separate existence. The fact, however, may now be taken as thoroughly established, that, at the moment of combustion of hydrogen or of the hydrogen compounds, hydrogen peroxide is always formed, and not only so, but in all probability its formation invariably precedes the formation of water. This was to be expected as a consequence of the law of Avogadro and Gerhardt, which leads us to expect this sequence in the case of equal interactions of volumes of vapours and gases; and in hydrogen peroxide we actually have such equal volumes of the elementary gases.

The instability of hydrogen peroxide—that is to say, the ease with which it decomposes into water and oxygen, even at the mere contact of porous substances—accounts for the circumstance that it does not form a permanent product of combustion, and is not produced during the decomposition of water. I may mention this additional consideration that, with respect

to hydrogen peroxide, we may look for its effecting still further substitutions of hydrogen by means of which we may expect to obtain still more highly oxidised water compounds, such as H_2O_3 and H_2O_4. These Schönbein and Bunsen have long been seeking, and Berthelot is investigating them at present. It is probable, however, that the reaction will stop at the last compound, because we find that, in a number of cases, the addition of four atoms of oxygen seems to form a limit. Thus, OsO_4, $KClO_4$, $KMnO_4$, K_2SO_4, Na_3PO_4, and such like, represent the highest grades of oxidation.[1]

As for the last forty years, from the times of Berzelius, Dumas, Liebig, Gerhardt, Williamson, Frankland, Kolbe, Kekulé, and Butleroff, most theoretical generalisations have centred round organic or carbon compounds, so we will, for the sake of brevity, leave out the discussion of ammonia derivatives, notwithstanding their simplicity with respect to the doctrine of substitutions; we will dwell more especially on its application to carbon compounds, starting from methane, CH_4, as the simplest of the hydrocarbons, containing in its molecule one atom of carbon. According to the principles enumerated we may derive from CH_4 every combination of the form CH_3X, CH_2X_2, CHX_3, and CX_4, in which X is an element, or radicle, equivalent to hydrogen—that is to say, competent to take its place or to combine with it. Such are the chlorine substitutes mentioned already, such is wood-spirit, $CH_3(OH)$, in which X is represented by the residue of water, and such are numerous other carbon derivatives. If we continue, with the aid of hydroxyl, further substitutions of the hydrogen of methane we shall obtain successively $CH_2(OH)_2$, $CH(OH)_3$, and $C(OH)_4$. But if, in proceeding thus, we bear in mind that $CH_2(OH)_2$ contains two hydroxyls in the same form as hydrogen peroxide, H_2O_2 or $(OH)_2$, contains them—and moreover not only in one molecule, but together, attached to one and the same atom of carbon—so here we must look for the same decomposition as that which we find in hydrogen peroxide, and accompanied also by the formation of water as an independently existing molecule; therefore $CH_2(OH)_2$ should yield, as it actually does, immediately water and the oxide of methylene, CH_2O, which is methane with

[1] Because more than four atoms of hydrogen never unite with one atom of the elements, and because the hydrogen compounds (*e.g.* HCl, H_2S, H_3P, H_4Si) always form their highest oxides with four atoms of oxygen, and as the highest forms of oxides (OsO_4, RuO_4) also contain four of oxygen, and eight groups of the periodic system, corresponding to the highest basic oxides R_2O, RO, R_2O_3, RO_2, R_2O_5, RO_3, R_2O_7, and RO_4, imply the above relationship, and because of the nearest analogues among the elements—such as Mg, Zn, Cd, and Hg; or Cr, Mo, W, and U; or Si, Ge, Sn, and Pt; or F, Cl, Br, and I, and so forth—not more than four are known, it seems to me that in these relationships there lies a deep interest and meaning with regard to chemical mechanics. But because, to my imagination, the idea of unity of design in Nature, either acting in complex celestial systems or among chemical molecules, is very attractive, especially because the atomic teaching at once acquires its true meaning, I will recall the following facts relating to the solar system. There are eight major planets, of which the four inner ones are not only separated from the four outer by asteroids, but differ from them in many respects, as, for example, in the smallness of their diameters and their greater density. Saturn with his ring has eight satellites, Jupiter and Uranus have each four. It is evident that in the solar systems also we meet with these higher numbers four and eight which appear in the combination of chemical molecules.

oxygen substituted for two atoms of hydrogen. Exactly in the same manner out of $CH(OH)_3$ are formed water and formic acid, CHO(OH), and out of $C(OH)_4$ is produced water and carbonic acid, or directly carbonic anhydride, CO_2, which will therefore be nothing else than methane with the double replacement of pairs of hydrogen by oxygen. As nothing leads to the supposition that the four atoms of hydrogen in methane differ one from the other, so it does not matter by what means we obtain any one of the combinations indicated—they will be identical; that is to say, there will be no case of actual isomerism, although there may easily be such cases of isomerism as have been distinguished by the term metamerism.

Formic acid, for example, has two atoms of hydrogen, one attached to the carbon left from the methane, and the other attached to the oxygen which has entered in the form of hydroxyl, and if one of them be replaced by some substance X it is evident that we shall obtain substances of the same composition, but of different construction, or of different orders of movement among the molecules, and therefore endowed with other properties and reactions. If X be methyl, CH_3—that is to say, a group capable of replacing hydrogen because it is actually contained with hydrogen in methane itself—then by substituting this group for the original hydrogen we obtain acetic acid, $CCH_3O(OH)$, out of formic, and by substitution of the hydrogen in its oxide or hydroxyl we obtain methyl formate, $CHO(OCH_3)$. These substances differ so much from each other physically and chemically that at first sight it is hardly possible to admit that they contain the same atoms in identically the same proportions. Acetic acid, for example, boils at a higher temperature than water, and has a higher specific gravity than it, whilst its metameride, methyl formate, is lighter than water, and boils at 30°—that is to say, it evaporates very easily.

Let us now turn to carbon compounds containing two atoms of carbon to the molecule, as in acetic acid, and proceed to evolve them from methane by the principle of substitution. This principle declares at once that methane can only be split up in the four following ways:—

1. Into a group CH_3 equivalent with H. Let us call changes of this nature methylation.

2. Into a group CH_2 and H_2. We will call this order of substitutions methylenation.

3. Into CH and H_3, which commutations we will call acetylenation.

4. Into C and H_4, which may be called carbonation.

It is evident that hydrocarbon compounds containing two atoms of carbon can only proceed from methane, CH_4, which contains four atoms of hydrogen by the first three methods of substitution; carbonation would yield free carbon if it could take place directly, and if the molecule of free carbon—which is in reality very complex, that is to say strongly polyatomic, as I have long since been proving by various means—could contain only C_2 like the molecules O_2, H_2, N_2, and so on.

By methylation we should evidently obtain from marsh gas, ethane, $CH_3CH_3 = C_2H_6$.

By methylenation—that is, by substituting group CH_2 for H_2—methane forms ethylene, $CH_2CH_2 = C_2H_4$.

By acetylenation—that is, by substituting three atoms of hydrogen, H_3, in methane—by the remnant CH, we get acetylene, $CHCH = C_2H_2$.

If we have applied the principles of Newton correctly, there should not be any other hydrocarbons containing two atoms of carbon in the molecule. All these combinations have long been known, and in each of them we can not only produce those substitutions of which an example has been given in the case of methane, but also all the phases of other substitutions, as we shall find from a few more instances, by the aid of which I trust that I shall be able to show the great complexity of those derivatives which, on the principle of substitution, can be obtained from each hydrocarbon. Let us content ourselves with the case of ethane, CH_3CH_3, and the substitution of the hydrogen by hydroxyl. The following are the possible changes:—

1. $CH_3CH_2(OH)$: this is nothing more than spirit of wine, or ethyl alcohol, $C_2H_5(OH)$ or C_2H_6O.

2. $CH_2(OH)CH_2(OH)$: this is the glycol of Würtz, which has shed so much light on the history of alcohol. Its isomeride may be $CH_3CH(OH)_2$, but as we have seen in the case of $CH(OH)_2$, it decomposes, giving off water, and forming aldehyde, CH_3CHO, a substance capable of yielding alcohol by uniting with hydrogen, and of yielding acetic acid by uniting with oxygen.

If glycol, $CH_2(OH)CH_2(OH)$, loses its water, it may be seen at once that it will not now yield aldehyde, CH_3CHO, but its isomeride, $\overset{CH_2CH_2}{O}$, the oxide of ethylene. I have here indicated in a special manner the oxygen which has taken the place of two atoms of the hydrogen of ethane taken from different atoms of the carbon.

3. $CH_3C(OH)_3$ decomposed as $CH(OH)_3$, forming water and acetic acid, $CH_3CO(OH)$. It is evident that this acid is nothing else than formic acid, $CHO(OH)$, with its hydrogen replaced by methyl. Without examining further the vast number of possible derivatives, I will direct your attention to the circumstance that in dissolving acetic acid in water we obtain the maximum contraction and the greatest viscosity when to the molecule $CH_3CO(OH)$ is added a molecule of water, which is the proportion which would form the hydrate $CH_3C(OH)_3$. It is probable that the doubling of the molecule of acetic acid at temperatures approaching its boiling-point has some connection with this power of uniting with one molecule of water.

4. $CH_2(OH)C(OH)_3$ is evidently an alcoholic acid, and indeed this compound, after losing water, answers to glycolic acid, $CH_2(OH)CO(OH)$. Without investigating all the possible isomerides, we will note only that the hydrate $CH(OH)_2CH(OH)_2$ has the same composition as $CH_2(OH)C(OH)_3$, and although corresponding to glycol, and being a symmetrical substance, it becomes, on parting with its water, the aldehyde of oxalic acid, or the glyoxal of Debus, CHOCHO.

5. $CH(OH)_2C(OH_3)$, from the tendency of all the preceding, corresponds with glyoxylic acid, an aldehyde acid, $CHOCO(OH)$, because the group $CO(OH)$, or carboxyl, enters into the compositions of organic acids, and the group CHO defines the aldehyde function.

6. $C(OH)_3C(OH)_3$ through the loss of $2H_2O$ yields the bibasic oxalic acid

$CO(OH)CO(OH)$, which generally crystallises with $2H_2O$, following thus the normal type of hydration characteristic of ethane.[2]

Thus, by applying the principle of substitution, we can, in the simplest manner, derive not only every kind of hydrocarbon compound, such as the alcohols, the aldehyde-alcohols, aldehydes, alcohol-acids, and the acids, but also combinations analogous to hydrated crystals which usually are disregarded.

But even those unsaturated substances, of which ethylene, CH_2CH_2, and acetylene, CHCH, are types, may be evolved with equal simplicity. With respect to the phenomena of isomerism, there are many possibilities among the hydrocarbon compounds containing two atoms of carbon, and without going into details it will be sufficient to indicate that the following formulæ, though not identical, will be isomeric substantially among themselves:— CH_3CHX_2 and CH_2XCH_2X, although both contain $C_2H_4X_2$; or CH_2CX_2 and CHXCHX, although both contain $C_2H_2X_2$, if by X we indicate chlorine or generally an element capable of replacing one atom of hydrogen, or capable of uniting with it. To isomerism of this kind belongs the case of aldehyde and the oxide of ethylene, to which we have already referred, because both have the composition C_2H_4O.

What I have said appears to me sufficient to show that the principle of substitution adequately explains the composition, the isomerism, and all the diversity of combination of the hydrocarbons, and I shall limit the further development of these views to preparing a complete list of every possible hydrocarbon compound containing three atoms of carbon in the molecule. There are eight in all, of which only five are known at present.[3]

Among those possible for C_3H_6 there should be two isomerides, propylene and trimethylene, and they are both already known. For C_3H_4 there should be three isomerides: allylene and allene are known, but the third has not yet been discovered; and for C_3H_2 there should be two isomerides, though

[2] One more isomeride, $CH_2CH(OH)$, is possible—that is, secondary vinyl alcohol, which is related to ethylene, CH_2CH_2, but derived by the principle of substitution from CH_4. Other isomerides, of the composition C_2H_4O, such, for example, as $CCH_3(OH)$, are impossible, because it would correspond with the hydrocarbon $CHCH_3 = C_2H_4$, which is isomeric with ethylene, and it cannot be derived from methane. If such an isomeride existed it would be derived from CH_2, but such products are, up to the present, unknown. In such cases the insufficiency of the points of departure of the statical structural teaching is shown. It first admits constant atomicity and then rejects it, the facts serving to establish either one or the other view; and therefore it seems to me that we must come to the conclusion that the structural method of reasoning, having done a service to science, has outlived the age, and must be regenerated, as in their time was the teaching of the electro-chemists, the radicalists, and the adherents of the doctrine of types. As we cannot now lean on the views above stated, it is time to abandon the structural theory. They will all be united in chemical mechanics, and the principle of substitution must be looked on only as a preparation for the coming epoch in chemistry, where such cases as the isomerism of fumaric and maleic acids, when explained dynamically, as proposed by Le Bel and Van't Hoff, may yield points of departure.

[3] Conceding variable atomicity, the structuralists must expect an incomparably larger number of isomerides, and they cannot now decline to acknowledge the change of atomicity, were it only for the examples HgCl and $HgCl_2$, CO and CO_2, PCl_3 and PCl_5.

neither of them is known as yet. Their composition and structure is easily deduced from ethane, ethylene, and acetylene, by methylation, by methylenation, by acetylenation and by carbonation.

1. $C_3H_8 = CH_3CH_2CH_3$ out of CH_3CH_3 by methylation. This hydrocarbon is named propane.

2. $C_3H_6 = CH_3CHCH_2$ out of CH_3CH_3 by methylenation. This substance is propylene.

3. $C_3H_6 = CH_2CH_2CH_2$ out of CH_3CH_3 by methylenation. This substance is trimethylene.

4. $C_3H_4 = CH_3CCH$ out of CH_3CH_3 by acetylenation or from CHCH by methylation. This hydrocarbon is named allylene.

5. $C_3H_4 = \begin{matrix}CHCH\\CH_2\end{matrix}$ out of CH_3CH_3 by acetylenation, or from CH_2CH_2 by methylenation, because $\begin{matrix}CH_2CH\\CH\end{matrix} = \begin{matrix}CHCH\\CH_2\end{matrix}$. This body is as yet unknown.

6. $C_3H_4 = CH_2CCH_2$ out of CH_2CH_2 by methylenation. This hydrocarbon is named allene, or iso-allylene.

7. $C_3H_2 = \begin{matrix}CHCH\\C\end{matrix}$ out of CH_3CH_3 by symmetrical carbonation, or out of CH_2CH_2 by acetylenation. This compound is unknown.

8. $C_3H_2 = \begin{matrix}CC\\CH_2\end{matrix}$ out of CH_3CH_3 by carbonation, or out of CHCH by methylenation. This compound is unknown.

If we bear in mind that for each hydrocarbon serving as a type in the above tables there are a number of corresponding derivatives, and that every compound obtained may, by further methylation, methylenation, acetylenation, and carbonation, produce new hydrocarbons, and these may be followed by a numerous suite of derivatives and an immense number of isomeric substances, it is possible to understand the limitless number of carbon compounds, although they all have the one substance, methane, for their origin. The number of substances is so enormous that it is no longer a question of enlarging the possibilities of discovery, but rather of finding some means of testing them analogous to the well-known two which for a long time have served as gauges for all carbon compounds.

I refer to the law of even numbers and to that of limits, the first enunciated by Gerhardt some forty years ago, with respect to hydrocarbons, namely, that their molecules always contain an even number of atoms of hydrogen. But by the method which I have used of deriving all the hydrocarbons from methane, CH_4, this law may be deduced as a direct consequence of the principle of substitutions. Accordingly, in methylation, CH_3 takes the place of H, and therefore CH_2 is added. In methylenation the number of atoms of hydrogen remains unchanged, and at each acetylenation it is reduced by two, and in carbonation by four, atoms—that is to say, an even number of atoms of hydrogen is always added or removed. And because the fundamental hydrocarbon, methane, CH_4, contains an even number of atoms of hydrogen, therefore all its derivative hydrocarbons will also contain even numbers of hydrogen, and this constitutes the law of even numbers.

The principle of substitutions explains with equal simplicity the conception of the limiting compositions of hydrocarbons C_nH_{2n+2}, which I derived, in

1861,[4] in an empirical manner from accumulated materials available at that time, and on the basis of the limits to combinations worked out by Dr. Frankland for other elements.

Of all the various substitutions the highest proportion of hydrogen is yielded by methylation, because in that operation alone does the quantity of hydrogen increase; therefore, taking methane as a point of departure, if we imagine methylation effected $(n-1)$ times we obtain hydrocarbon compounds containing the highest quantities of hydrogen. It is evident that they will contain $CH_4 + (n-1)CH_2$, or C_nH_{2n+2}, because methylation leads to the addition of CH_2 to the compound.

It will thus be seen that by the principle of substitution—that is to say, by the third law of Newton—we are able to deduce, in the simplest manner, not only the individual composition, the isomerism, and relations of substances, but also the general laws which govern their most complex combinations, without having recourse either to statical constructions, to the definition of atomicities, to the exclusion of free affinities, or to the recognition of those single, double, or treble bonds which are so indispensable to structuralists in the explanation of the composition and construction of hydrocarbon compounds. And yet, by the application of the dynamical principles of Newton, we can attain to that chief and fundamental object, the comprehension of isomerism in hydrocarbon compounds, and the forecasting of the existence of combinations as yet unknown, by which the edifice raised by structural teaching is strengthened and supported. Besides—and I count this for a circumstance of special importance—the process which I advocate will make no difference in those special cases which have been already so well worked out, such as, for example, the isomerism of the hydrocarbons and alcohols, even to the extent of not interfering with the nomenclature which has been adopted, and the structural system will retain all the glory of having worked up, in a thoroughly scientific manner, the store of information which Gerhardt had accumulated about the middle of the fifties, and the still higher glory of establishing the rational synthesis of organic substances. Nothing will be lost to the structural doctrine except its statical origin; and as soon as it will embrace the dynamic principles of Newton, and suffer itself to be guided by them, I believe that we shall attain for chemistry that unity of principle which is now wanting. Many an adept will be attracted to that brilliant and fascinating enterprise, the penetration into the unseen world of the kinetic relations of atoms, to the study of which the last twenty-five years have contributed so much labour and such high inventive faculties.

D'Alembert found in mechanics that if inertia be taken to represent force, dynamic equations may be applied to statical questions, which are thereby rendered more simple and more easily understood.

The structural doctrine in chemistry has unconsciously followed the same course, and therefore its terms are easily adopted; they may retain their present forms provided that a truly dynamical—that is to say, Newtonian—meaning be ascribed to them.

Before finishing my task and demonstrating the possibility of adapting

[4] 'Essai d'une théorie sur les limites des combinaisons organiques,' par D. Mendeléeff, 2/11 août 1861, *Bulletin de l'Académie i. d. Sc. de St. Pétersbourg*, t. v.

structural doctrines to the dynamics of Newton, I consider it indispensable to touch on one question which naturally arises, and which I have heard discussed more than once. If bromine, the atom of which is eighty times heavier than that of hydrogen, takes the place of hydrogen, it would seem that the whole system of dynamic equilibrium must be destroyed.

Without entering into the minute analysis of this question, I think it will be sufficient to examine it by the light of two well-known phenomena, one of which will be found in the department of chemistry and the other in that of celestial mechanics, and both will serve to demonstrate the existence of that unity in the plan of creation which is a consequence of the Newtonian doctrines. Experiments demonstrate that when a heavy element is substituted for a light one in a chemical compound—for example, for magnesium, in the oxide of that metal, an atom of mercury, which is 8½ times heavier—the chief chemical characteristics or properties are generally, though not always, preserved.

The substitution of silver for hydrogen, than which it is 108 times heavier, does not affect all the properties of the substance, though it does some. Therefore chemical substitutions of this kind—the substitution of light for heavy atoms—need not necessarily entail changes in the original equilibrium; and this point is still further elucidated by the consideration that the periodic law indicates the degree of influence of an increment of weight in the atom as affecting the possible equilibria, and also what degree of increase in the weight of the atoms reproduces some, though not all, of the properties of the substance.

This tendency to repetition—these periods—may be likened to those annual or diurnal periods with which we are so familiar on the earth. Days and years follow each other, but, as they do so, many things change; and in like manner chemical evolutions, changes in the masses of the elements, permit of much remaining undisturbed, though many properties undergo alteration. The system is maintained according to the laws of conservation in nature, but the motions are altered in consequence of the change of parts.

Next, let us take an astronomical case—such, for example, as the earth and the moon—and let us imagine that the mass of the latter is constantly increasing. The question is, what will then occur? The path of the moon in space is a wave-line similar to that which geometricians have named epicycloidal, or the locus of a point in a circle rolling round another circle. But in consequence of the influence of the moon it is evident that the path of the earth itself cannot be a geometric ellipse, even supposing the sun to be immovably fixed; it must be an epicycloidal curve, though not very far removed from the true ellipse—that is to say, it will be impressed with but faint undulations. It is only the common centre of gravity of the earth and the moon which describes a true ellipse round the sun. If the moon were to increase, the relative undulations of the earth's path would increase in amplitude, those of the moon would also change, and when the mass of the moon had increased to an equality with that of the earth, the path would consist of epicycloidal curves crossing each other, and having opposite phases. But a similar relation exists between the sun and the earth, because the former is also moving in space. We may apply these views to the world of atoms, and

suppose that in their movements, when heavy ones take the place of those that are lighter, similar changes take place, provided that the system or the molecule is preserved throughout the change.

It seems probable that in the heavenly systems, during incalculable astronomical periods, changes have taken place and are still going on similar to those which pass rapidly before our eyes during the chemical reaction of molecules, and the progress of molecular mechanics may—we hope will—in course of time permit us to explain those changes in the stellar world which have more than once been noticed by astronomers, and which are now so carefully studied. A coming Newton will discover the laws of these changes. Those laws, when applied to chemistry, may exhibit peculiarities, but these will certainly be mere variations on the grand harmonious theme which reigns in nature. The discovery of the laws which produce this harmony in chemical evolution will only be possible, it seems to me, under the banner of Newtonian dynamics, which has so long waved over the domains of mechanics, astronomy, and physics. In calling chemists to take their stand under its peaceful and catholic shadow I imagine that I am aiding in establishing that scientific union which the managers of the Royal Institution wish to effect, who have shown their desire to do so by the flattering invitation which has given me—a Russian—the opportunity of laying before the countrymen of Newton an attempt to apply to chemistry one of his immortal principles.

APPENDIX II.

THE PERIODIC LAW OF THE CHEMICAL ELEMENTS.

BY PROFESSOR MENDELÉEFF.

FARADAY LECTURE DELIVERED BEFORE THE FELLOWS OF THE CHEMICAL SOCIETY IN THE THEATRE OF THE ROYAL INSTITUTION, ON TUESDAY, JUNE 4, 1889.

THE high honour bestowed by the Chemical Society in inviting me to pay a tribute to the world-famed name of Faraday by delivering this lecture has induced me to take for its subject the Periodic Law of the Elements—this being a generalisation in chemistry which has of late attracted much attention.

While science is pursuing a steady onward movement, it is convenient from time to time to cast a glance back on the route already traversed, and especially to consider the new conceptions which aim at discovering the general meaning of the stock of facts accumulated from day to day in our laboratories. Owing to the possession of laboratories, modern science now bears a new character, quite unknown, not only to antiquity, but even to the preceding century. Bacon's and Descartes' idea of submitting the mechanism of science simultaneously to experiment and reasoning has been fully realised in the case of chemistry, it having become not only possible but always customary to experiment. Under the all-penetrating control of experiment, a new theory, even if crude, is quickly strengthened, provided it be founded on a sufficient basis; the asperities are removed, it is amended by degrees, and soon loses the phantom light of a shadowy form or of one founded on mere prejudice; it is able to lead to logical conclusions, and to submit to experimental proof. Willingly or not, in science we all must submit not to what seems to us attractive from one point of view or from another. but to what represents an agreement between theory and experiment; in other words, to demonstrated generalisation and to the approved experiment. Is it long since many refused to accept the generalisations involved in the law of Avogadro and Ampère, so widely extended by Gerhardt? We still may hear the voices of its opponents; they enjoy perfect freedom, but vainly will their voices rise so long as they do not use the language of demonstrated facts.

The striking observations with the spectroscope which have permitted us to analyse the chemical constitution of distant worlds, seemed, at first, applicable to the task of determining the nature of the atoms themselves; but the working out of the idea in the laboratory soon demonstrated that the characters of spectra are determined, not directly by the atoms, but by the molecules into which the atoms are packed; and so it became evident that more verified facts must be collected before it will be possible to formulate new generalisations capable of taking their place beside those ordinary ones based upon the conception of simple substances and atoms. But as the shade of the leaves and roots of living plants, together with the relics of a decayed vegetation, favour the growth of the seedling and serve to promote its luxurious development, in like manner sound generalisations—together with the relics of those which have proved to be untenable—promote scientific productivity, and ensure the luxurious growth of science under the influence of rays emanating from the centres of scientific energy. Such centres are scientific associations and societies. Before one of the oldest and most powerful of these I am about to take the liberty of passing in review the 20 years' life of a generalisation which is known under the name of the Periodic Law. It was in March 1869 that I ventured to lay before the then youthful Russian Chemical Society the ideas upon the same subject which I had expressed in my just written 'Principles of Chemistry.'

Without entering into details, I will give the conclusions I then arrived at in the very words I used:—

'1. The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties.

'2. Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (*e.g.* platinum, iridium, osmium) or which increase regularly (*e.g.* potassium, rubidium, cæsium).

'3. The arrangement of the elements, or of groups of elements, in the order of their atomic weights, corresponds to their so-called *valencies* as well as, to some extent, to their distinctive chemical properties—as is apparent, among other series, in that of lithium, beryllium, barium, carbon, nitrogen, oxygen, and iron.

'4. The elements which are the most widely diffused have *small* atomic weights.

'5. The *magnitude* of the atomic weight determines the character of the element, just as the magnitude of the molecule determines the character of a compound.

'6. We must expect the discovery of many yet *unknown* elements—for example, elements analogous to aluminium and silicon, whose atomic weight would be between 65 and 75.

'7. The atomic weight of an element may sometimes be amended by a knowledge of those of the contiguous elements. Thus, the atomic weight of tellurium must lie between 123 and 126, and cannot be 128.

'8. Certain characteristic properties of the elements can be foretold from their atomic weights.

'The aim of this communication will be fully attained if I succeed in drawing the attention of investigators to those relations which exist between the atomic weights of dissimilar elements, which, as far as I know, have hitherto been almost completely neglected. I believe that the solution of some of the most important problems of our science lies in researches of this kind.'

To-day, twenty years after the above conclusions were formulated, they may still be considered as expressing the essence of the now well-known periodic law.

Reverting to the epoch terminating with the sixties, it is proper to indicate three series of data without the knowledge of which the periodic law could not have been discovered, and which rendered its appearance natural and intelligible.

In the first place, it was at that time that the numerical value of atomic weights became definitely known. Ten years earlier such knowledge did not exist, as may be gathered from the fact that in 1860 chemists from all parts of the world met at Karlsruhe in order to come to some agreement, if not with respect to views relating to atoms, at any rate as regards their definite representation. Many of those present probably remember how vain were the hopes of coming to an understanding, and how much ground was gained at that Congress by the followers of the unitary theory so brilliantly represented by Cannizzaro. I vividly remember the impression produced by his speeches, which admitted of no compromise, and seemed to advocate truth itself, based on the conceptions of Avogadro, Gerhardt, and Regnault, which at that time were far from being generally recognised. And though no understanding could be arrived at, yet the objects of the meeting were attained, for the ideas of Cannizzaro proved, after a few years, to be the only ones which could stand criticism, and which represented an atom as—'the smallest portion of an element which enters into a molecule of its compound.' Only such real atomic weights—not conventional ones—could afford a basis for generalisation. It is sufficient, by way of example, to indicate the following cases in which the relation is seen at once and is perfectly clear:—

K = 39	Rb = 85	Cs = 133
Ca = 40	Sr = 87	Ba = 137

whereas with the equivalents then in use—

K = 39	Rb = 85	Cs = 133
Ca = 20	Sr = 43·5	Ba = 68·5

the consecutiveness of change in atomic weight, which with the true values is so evident, completely disappears.

Secondly, it had become evident during the period 1860–70, and even during the preceding decade, that the relations between the atomic weights of analogous elements were governed by some general and simple laws. Cooke, Cremers, Gladstone, Gmelin, Lenssen, Pettenkofer, and especially Dumas, had already established many facts bearing on that view. Thus Dumas compared the following groups of analogous elements with organic radicles:—

	Diff.		Diff.		Diff.		Diff.
		Mg = 12	8	P = 31	44	O = 8	8
Li = 7	16	Ca = 20	3 × 8	As = 75	44	S = 16	3 × 8
Na = 23	16	Sr = 44	3 × 8	Sb = 119	2 × 44	Se = 40	3 × 8
K = 39		Ba = 68		Bi = 207		Te = 64	

and pointed out some really striking relationships, such as the following:—

F = 19.
Cl = 35·5 = 19 + 16·5.
Br = 80 = 19 + 2 × 16·5 + 28.
I = 127 = 2 × 19 + 2 × 16·5 + 2 × 28.

A. Strecker, in his work 'Theorien und Experimente zur Bestimmung der Atomgewichte der Elemente' (Braunschweig, 1859), after summarising the data relating to the subject, and pointing out the remarkable series of equivalents—

Cr = 26·2 Mn = 27·6 Fe = 28 Ni = 29 Co = 30 Cu = 31·7
Zn = 32·5

remarks that: 'It is hardly probable that all the above-mentioned relations between the atomic weights (or equivalents) of chemically analogous elements are merely accidental. We must, however, leave to the future the discovery of the *law* of the relations which appears in these figures.'[1]

In such attempts at arrangement and in such views are to be recognised the real forerunners of the periodic law; the ground was prepared for it between 1860 and 1870, and that it was not expressed in a determinate form before the end of the decade may, I suppose, be ascribed to the fact that only analogous elements had been compared. The idea of seeking for a relation between the atomic weights of all the elements was foreign to the ideas then current, so that neither the *vis tellurique* of De Chancourtois, nor the *law of octaves* of Newlands, could secure anybody's attention. And yet both De Chancourtois and Newlands, like Dumas and Strecker, more than Lenssen and Pettenkofer, had made an approach to the periodic law and had discovered its germs. The solution of the problem advanced but slowly, because the facts, and not the law, stood foremost in all attempts; and the law could not awaken a general interest so long as elements, having no apparent connection with each other, were included in the same octave, as for example:—

1st octave of Newlands..	H	F	Cl	Co & Ni	Br	Pd	I	Pt & Ir
7th Ditto....	O	S	Fe	Se	Rh & Ru	Te	Au	Os or Th

Analogies of the above order seemed quite accidental, and the more so as the octave contained occasionally ten elements instead of eight, and when two

[1] 'Es ist wohl kaum anzunehmen, dass alle im Vorhergehenden hervorgehobenen Beziehungen zwischen den Atomgewichten (oder Aequivalenten) in chemischen Verhältnissen einander ähnliche Elemente bloss zufällig sind. Die Auffindung der in diesen Zahlen *gesetzlichen* Beziehungen müssen wir jedoch der Zukunft überlassen.'

such elements as Ba and V, Co and Ni, or Rh and Ru, occupied one place in the octave.[2] Nevertheless, the fruit was ripening, and I now see clearly that Strecker, De Chancourtois, and Newlands stood foremost in the way towards the discovery of the periodic law, and that they merely wanted the boldness necessary to place the whole question at such a height that its reflection on the facts could be clearly seen.

A third circumstance which revealed the periodicity of chemical elements was the accumulation, by the end of the sixties, of new information respecting the rare elements, disclosing their many-sided relations to the other elements and to each other. The researches of Marignac on niobium, and those of Roscoe on vanadium, were of special moment. The striking analogies between vanadium and phosphorus on the one hand, and between vanadium and chromium on the other, which became so apparent in the investigations connected with that element, naturally induced the comparison of V = 51 with Cr = 52, Nb = 94 with Mo = 96, and Ta = 192 with W = 194; while, on the other hand, P = 31 could be compared with S = 32, As = 75 with Se = 79, and Sb = 120 with Te = 125. From such approximations there remained but one step to the discovery of the law of periodicity.

The law of periodicity was thus a direct outcome of the stock of generalisations and established facts which had accumulated by the end of the decade 1860–1870: it is an embodiment of those data in a more or less sytematic expression. Where, then, lies the secret of the special importance which has since been attached to the periodic law, and has raised it to the position of a generalisation which has already given to chemistry unexpected aid, and which promises to be far more fruitful in the future and to impress upon several branches of chemical research a peculiar and original stamp? The remaining part of my communication will be an attempt to answer this question.

In the first place we have the circumstance that, as soon as the law made its appearance, it demanded a revision of many facts which were considered by chemists as fully established by existing experience. I shall return, later on, briefly to this subject, but I wish now to remind you that the periodic law, by insisting on the necessity for a revision of supposed facts, exposed itself at once to destruction in its very origin. Its first requirements, however, have been almost entirely satisfied during the last 20 years; the supposed facts have yielded to the law, thus proving that the law itself was a legitimate induction from the verified facts. But our inductions from data have often to do with such details of a science so rich in facts, that only generalisations which cover a wide range of important phenomena can attract general attention. What were the regions touched on by the periodic law? This is what we shall now consider.

The most important point to notice is, that periodic functions, used for the purpose of expressing changes which are dependent on variations of time and space, have been long known. They are familiar to the mind when we have to deal with motion in closed cycles, or with any kind of deviation from

[2] To judge from J. A. R. Newlands's work, *On the Discovery of the Periodic Law*, London, 1884, p. 149; 'On the Law of Octaves' (from the *Chemical News*, 12, 83, August 18, 1865).

a stable position, such as occurs in pendulum-oscillations. A like periodic function became evident in the case of the elements, depending on the mass of the atom. The primary conception of the masses of bodies, or of the masses of atoms, belongs to a category which the present state of science forbids us to discuss, because as yet we have no means of dissecting or analysing the conception. All that was known of functions dependent on masses derived its origin from Galileo and Newton, and indicated that such functions either decrease or increase with the increase of mass, like the attraction of celestial bodies. The numerical expression of the phenomena was always found to be proportional to the mass, and in no case was an increase of mass followed by a recurrence of properties such as is disclosed by the periodic law of the elements. This constituted such a novelty in the study of the phenomena of nature that, although it did not lift the veil which conceals the true conception of mass, it nevertheless indicated that the explanation of that conception must be searched for in the masses of the atoms; the more so, as all masses are nothing but aggregations, or additions, of chemical atoms which would be best described as chemical individuals. Let me remark, by the way, that though the Latin word 'individual' is merely a translation of the Greek word 'atom,' nevertheless history and custom have drawn so sharp a distinction between the two words, and the present chemical conception of atoms is nearer to that defined by the Latin word than by the Greek, although this latter also has acquired a special meaning which was unknown to the classics. The periodic law has shown that our chemical individuals display a harmonic periodicity of properties, dependent on their masses. Now natural science has long been accustomed to deal with periodicities observed in nature, to seize them with the vice of mathematical analysis, to submit them to the rasp of experiment. And these instruments of scientific thought would surely, long since, have mastered the problem connected with the chemical elements, were it not for a new feature which was brought to light by the periodic law, and which gave a peculiar and original character to the periodic function.

If we mark on an axis of abscissæ a series of lengths proportional to angles, and trace ordinates which are proportional to sines or other trigonometrical functions, we get periodic curves of a harmonic character. So it might seem, at first sight, that with the increase of atomic weights the function of the properties of the elements should also vary in the same harmonious way. But in this case there is no such continuous change as in the curves just referred to, because the periods do not contain the infinite number of points constituting a curve, but a *finite* number only of such points. An example will better illustrate this view. The atomic weights—

Ag = 108	Cd = 112	In = 113	Sn = 118	Sb = 120
	Te = 125	I = 127		

steadily increase, and their increase is accompanied by a modification of many properties which constitutes the essence of the periodic law. Thus, for example, the densities of the above elements decrease steadily, being respectively—

10·5	8·6	7·4	7·2	6·7	6·4	4·9

while their oxides contain an increasing quantity of oxygen—

$$Ag_2O \quad Cd_2O_2 \quad In_2O_3 \quad Sn_2O_4 \quad Sb_2O_5 \quad Te_2O_6 \quad I_2O_7$$

But to connect by a curve the summits of the ordinates expressing any of these properties would involve the rejection of Dalton's law of multiple proportions. Not only are there no intermediate elements between silver, which gives AgCl, and cadmium, which gives $CdCl_2$, but, according to the very essence of the periodic law, there can be none; in fact a uniform curve would be inapplicable in such a case, as it would lead us to expect elements possessed of special properties at any point of the curve. The periods of the elements have thus a character very different from those which are so simply represented by geometers. They correspond to points, to numbers, to sudden changes of the masses, and not to a continuous evolution. In these sudden changes destitute of intermediate steps or positions, in the absence of elements intermediate between, say, silver and cadmium, or aluminium and silicon, we must recognise a problem to which no direct application of the analysis of the infinitely small can be made. Therefore, neither the trigonometrical functions proposed by Ridberg and Flavitzky, nor the pendulum-oscillations suggested by Crookes, nor the cubical curves of the Rev. Mr. Haughton, which have been proposed for expressing the periodic law, from the nature of the case, can represent the periods of the chemical elements. If geometrical analysis is to be applied to this subject, it will require to be modified in a special manner. It must find the means of representing in a special way, not only such long periods as that comprising,

K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br,

but short periods like the following:—

Na Mg Al Si P S Cl.

In the theory of numbers only do we find problems analogous to ours, and two attempts at expressing the atomic weights of the elements by algebraic formulæ seem to be deserving of attention, although neither of them can be considered as a complete theory, nor as promising finally to solve the problem of the periodic law. The attempt of E. J. Mills (1886) does not even aspire to attain this end. He considers that all atomic weights can be expressed by a logarithmic function,

$$15(n - 0{\cdot}9375^t),$$

in which the variables n and t are *whole numbers*. Thus, for oxygen, $n = 2$, and $t = 1$, whence its atomic weight is = 15·94; in the case of chlorine, bromine, and idione, n has respective values of 3, 6, and 9, whilst $t = 7$, 6, and 9; in the case of potassium, rubidium, and cæsium, $n = 4$, 6, and 9, and $t = 14$, 18, and 20.

Another attempt was made in 1888 by B. N. Tchitchérin. Its author places the problem of the periodic law in the first rank, but as yet he has investigated the alkali metals only. Tchitchérin first noticed the simple

relations existing between the atomic volumes of all alkali metals; they can be expressed, according to his views, by the formula

$$A(2 - 0{\cdot}00535An),$$

where A is the atomic weight, and n is equal to 8 for lithium and sodium, to 4 for potassium, to 3 for rubidium, and to 2 for cæsium. If n remained equal to 8 during the increase of A, then the volume would become zero at $A = 46\frac{2}{3}$, and it would reach its maximum at $A = 23\frac{1}{3}$. The close approximation of the number $46\frac{2}{3}$ to the differences between the atomic weights of analogous elements (such as Cs – Rb, I – Br, and so on); the close correspondence of the number $23\frac{1}{3}$ to the atomic weight of sodium; the fact of n being necessarily a whole number, and several other aspects of the question, induce Tchitchérin to believe that they afford a clue to the understanding of the nature of the elements; we must, however, await the full development of his theory before pronouncing judgment on it. What we can at present only be certain of is this: that attempts like the two above named must be repeated and multiplied, because the periodic law has clearly shown that the masses of the atoms increase abruptly, by steps, which are clearly connected in some way with Dalton's law of multiple proportions; and because the periodicity of the elements finds expression in the transition from RX to RX_2, RX_3, RX_4, and so on till RX_8, at which point, the energy of the combining forces being exhausted, the series begins anew from RX to RX_2, and so on.

While connecting by new bonds the theory of the chemical elements with Dalton's theory of multiple proportions, or atomic structure of bodies, the periodic law opened for natural philosophy a new and wide field for speculation. Kant said that there are in the world 'two things which never cease to call for the admiration and reverence of man: the moral law within ourselves, and the stellar sky above us.' But when we turn our thoughts towards the nature of the elements and the periodic law, we must add a third subject, namely, 'the nature of the elementary individuals which we discover everywhere around us.' Without them the stellar sky itself is inconceivable; and in the atoms we see at once their peculiar individualities, the infinite multiplicity of the individuals, and the submission of their seeming freedom to the general harmony of Nature.

Having thus indicated a new mystery of Nature, which does not yet yield to rational conception, the periodic law, together with the revelations of spectrum analysis, have contributed to again revive an old but remarkably long-lived hope—that of discovering, if not by experiment, at least, by a mental effort, the *primary matter*—which had its genesis in the minds of the Grecian philosophers, and has been transmitted, together with many other ideas of the classic period, to the heirs of their civilisation. Having grown, during the times of the alchemists up to the period when experimental proof was required, the idea has rendered good service; it induced those careful observations and experiments which later on called into being the works of Scheele, Lavoisier, Priestley, and Cavendish. It then slumbered awhile, but was soon awakened by the attempts either to confirm or to refute the ideas of Prout as to the multiple proportion relationship of the atomic

weights of all the elements. And once again the inductive or experimental method of studying Nature gained a direct advantage from the old Pythagorean idea: because atomic weights were determined with an accuracy formerly unknown. But again the idea could not stand the ordeal of experimental test, yet the prejudice remains and has not been uprooted, even by Stas; nay, it has gained a new vigour, for we see that all which is imperfectly worked out, new and unexplained, from the still scarcely studied rare metals to the hardly perceptible nebulæ, have been used to justify it. As soon as spectrum analysis appears as a new and powerful weapon of chemistry, the idea of a primary matter is immediately attached to it. From all sides we see attempts to constitute the imaginary substance *helium*[3] the so much longed for primary matter. No attention is paid to the circumstance that the helium line is only seen in the spectrum of the solar protuberances, so that its universality in Nature remains as problematic as the primary matter itself; nor to the fact that the helium line is wanting amongst the Fraunhofer lines of the solar spectrum, and thus does not answer to the brilliant fundamental conception which gives its real force to spectrum analysis.

And finally, no notice is even taken of the indubitable fact that the brilliancies of the spectral lines of the simple substances vary under different temperatures and pressures; so that all probabilities are in favour of the helium line simply belonging to some long since known element placed under such conditions of temperature, pressure, and gravity as have not yet been realised in our experiments. Again, the idea that the excellent investigations of Lockyer of the spectrum of iron can be interpreted in favour of the compound nature of that element, evidently must have arisen from some misunderstanding. The spectrum of a compound certainly does not appear as a sum of the spectra of its components; and therefore the observations of Lockyer can be considered precisely as a proof that iron undergoes no other changes at the temperature of the sun than those which it experiences in the voltaic arc—provided the spectrum of iron is preserved. As to the shifting of some of the lines of the spectrum of iron while the other lines maintain their positions, it can be explained, as shown by M. Kleiber ('Journal of the Russian Chemical and Physical Society,' 1885, 147), by the relative motion of the various strata of the sun's atmosphere, and by Zöllner's laws of the relative brilliancies of different lines of the spectrum. Moreover, it ought not to be forgotten that if iron were really proved to consist of two or more unknown elements, we should simply have an increase in the number of our elements—not a reduction, and still less a reduction of all of them to one single primary matter.

Feeling that spectrum analysis will not yield a support to the Pythagorean conception, its modern promoters are so bent upon its being confirmed by the periodic law, that the illustrious Berthelot, in his work 'Les origines de l'Alchimie,' 1885, 313, has simply mixed up the fundamental idea of the law of periodicity with the ideas of Prout, the alchemists, and Democritus about primary matter.[4] But the periodic law, based as it is on the solid and whole-

[3] That is, a substance having a wave-length equal to 0·0005875 millimetre.

[4] He maintains (on p. 309) that the periodic law requires two new analogous elements, having atomic weights of 48 and 64, occupying positions between sulphur

some ground of experimental research, has been evolved independently of any conception as to the nature of the elements; it does not in the least originate in the idea of a unique matter; and it has no historical connection with that relic of the torments of classical thought, and therefore it affords no more indication of the unity of matter or of the compound character of our elements, than the law of Avogadro, or the law of specific heats, or even the conclusions of spectrum analysis. None of the advocates of a unique matter have ever tried to explain the law from the standpoint of ideas taken from a remote antiquity when it was found convenient to admit the existence of many gods—and of a unique matter.

When we try to explain the origin of the idea of a unique primary matter, we easily trace that in the absence of inductions from experiment it derives its origin from the scientifically philosophical attempt at discovering some kind of unity in the immense diversity of individualities which we see around. In classical times such a tendency could only be satisfied by conceptions about the immaterial world. As to the material world, our ancestors were compelled to resort to some hypothesis, and they adopted the idea of unity in the formative material, because they were not able to evolve the conception of any other possible unity in order to connect the multifarious relations of matter. Responding to the same legitimate scientific tendency, natural science has discovered throughout the universe a unity of plan, a unity of forces, and a unity of matter, and the convincing conclusions of modern science compel every one to admit these kinds of unity. But while we admit unity in many things, we none the less must also explain the individuality and the apparent diversity which we cannot fail to trace everywhere. It has been said of old, 'Give a fulcrum, and it will become easy to displace the earth.' So also we must say, 'Give anything that is individualised, and the apparent diversity will be easily understood.' Otherwise, how could unity result in a multitude?

After a long and painstaking research, natural science has discovered the individualities of the chemical elements, and therefore it is now capable not only of analysing, but also of synthesising; it can understand and grasp the general and unity, as well as the individualised and the multitudinous. Unity and the general, like time and space, like force and motion, vary uniformly; the uniform admit of interpolations, revealing every intermediate phase. But the multitudinous, the individualised—like ourselves, like the chemical elements, like the members of a peculiar periodic function of elements, like Dalton's multiple proportions—is characterised in another way: we see in it, side by side with a connecting general principle, leaps, breaks of continuity, points which escape from the analysis of the infinitely small—a complete absence of intermediate links. Chemistry has found an answer to the question as to the causes of multitudes; and while retaining the conception of many elements, all submitted to the discipline of a general law, it offers an escape from the Indian Nirvana—the absorption in the universal, replacing it by the individualised. However, the place for indi-

and selenium, although nothing of the kind results from any of the different readings of the law.

viduality is so limited by the all-grasping, all-powerful universal, that it is merely a fulcrum for the understanding of multitude in unity.

Having touched upon the metaphysical bases of the conception of a unique matter which is supposed to enter into the composition of all bodies, I think it necessary to dwell upon another theory, akin to the above conception—the theory of the compound character of the elements now admitted by some—and especially upon one particular circumstance which, being related to the periodic law, is considered to be an argument in favour of that hypothesis.

Dr. Pelopidas, in 1883, made a communication to the Russian Chemical and Physical Society on the periodicity of the hydrocarbon radicles, pointing out the remarkable parallelism which was to be noticed in the change of properties of hydrocarbon radicles and elements when classed in groups. Professor Carnelley, in 1886, developed a similar parallelism. The idea of M. Pelopidas will be easily understood if we consider the series of hydrocarbon radicles which contain, say, 6 atoms of carbon:—

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
C_6H_{13}	C_6H_{12}	C_6H_{11}	C_6H_{10}	C_6H_9	C_6H_8	C_6H_7	C_6H_6

The first of these radicles, like the elements of the 1st group, combines with Cl, OH, and so on, and gives the derivatives of hexyl alcohol, $C_6H_{13}(OH)$; but, in proportion as the number of hydrogen atoms decreases, the capacity of the radicles of combining with, say, the halogens increases. C_6H_{12} already combines with 2 atoms of chlorine; C_6H_{11} with 3 atoms, and so on. The last members of the series comprise the radicles of acids; thus C_6H_8, which belongs to the 6th group, gives, like sulphur, a bibasic acid, $C_6H_8O_2(OH)_2$, which is homologous with oxalic acid. The parallelism can be traced still further, because C_6H_5 appears as a monovalent radicle of benzene, and with it begins a new series of aromatic derivatives, so analogous to the derivatives of the fat series. Let me also mention another example from among those which have been given by M. Pelopidas. Starting from the alkaline radicle of monomethylammonium, $N(CH_3)H_3$, or NCH_6, which presents many analogies with the alkaline metals of the 1st group, he arrives, by successively diminishing the number of the atoms of hydrogen, at a 7th group which contains cyanogen, CN, which has long since been compared to the halogens of the 7th group.

The most important consequence which, in my opinion, can be drawn from the above comparison is that the periodic law, so apparent in the elements, has a wider application than might appear at first sight; it opens up a new vista of chemical evolutions. But, while admitting the fullest parallelism between the periodicity of the elements and that of the compound radicles, we must not forget that in the periods of the hydrocarbon radicles we have a *decrease* of mass as we pass from the representatives of the first group to the next, while in the periods of the elements the mass *increases* during the progression. It thus becomes evident that we cannot speak of an identity of periodicity in both cases, unless we put aside the ideas of mass and attraction, which are the real corner-stones of the whole of natural science, and even enter into those very conceptions of simple substances which

came to light a full hundred years later than the immortal principles of Newton.[5]

From the foregoing, as well as from the failures of so many attempts at finding in experiment and speculation a proof of the compound character of the elements and of the existence of primordial matter, it is evident, in my opinion, that this theory must be classed among mere utopias. But utopias can only be combated by freedom of opinion, by experiment, and by new utopias. In the republic of scientific theories freedom of opinions is guaranteed. It is precisely that freedom which permits me to criticise openly the widely-diffused idea as to the unity of matter in the elements. Experiments and attempts at confirming that idea have been so numerous that it really would be instructive to have them all collected together, if only to serve as a warning against the repetition of old failures. And now as to new utopias which may be helpful in the struggle against the old ones, I do not think it quite useless to mention a *phantasy* of one of my students who imagined that the weight of bodies does not depend upon their mass, but upon the character of the motion of their atoms. The atoms, according to this new utopian, may all be homogeneous or heterogeneous, we know not which; we know them in motion only, and that motion they maintain with the same persistence as the stellar bodies maintain theirs. The weights of atoms differ only in consequence of their various modes and quantity of motion; the heaviest atoms may be much simpler than the lighter ones: thus an atom of mercury may be simpler than an atom of hydrogen—the manner in which it moves causes it to be heavier. My interlocutor even suggested that the view which attributes the greater complexity to the lighter elements finds confirmation in the fact that the hydrocarbon radicles mentioned by Pelopidas, while becoming lighter as they lose hydrogen, change their properties periodically in the same manner as the elements change theirs according as the atoms grow heavier.

The French proverb, *La critique est facile mais l'art est difficile*, however, may well be reversed in the case of all such ideal views, as it is much easier to formulate than to criticise them. Arising from the virgin soil of newly-established facts, the knowledge relating to the elements, to their masses, and to the periodic changes of their properties has given a motive for the formation of utopian hypotheses, probably because they could not be foreseen by the aid of any of the various metaphysical systems, and exist, like the idea of gravitation, as an independent outcome of natural science, requiring the acknowledgment of general laws, when these have been established with the same degree of persistency as is indispensable for the acceptance of a thoroughly established fact. Two centuries have elapsed since the theory of gravitation was enunciated, and although we do not understand its cause, we still must regard gravitation as a fundamental conception of natural philosophy, a conception which has enabled us to perceive much more than the metaphysicians did or could with their seeming omniscience. A hundred

[5] It is noteworthy that the year in which Lavoisier was born (1743)—the author of the idea of elements and of the indestructibility of matter—is later by exactly one century than the year in which the author of the theory of gravitation and mass was born (1643 N.S.). The affiliation of the ideas of Lavoisier and those of Newton is beyond doubt.

years later the conception of the elements arose; it made chemistry what it now is; and yet we have advanced as little in our comprehension of simple substances since the times of Lavoisier and Dalton as we have in our understanding of gravitation. The periodic law of the elements is only twenty years old; it is not surprising, therefore, that, knowing nothing about the causes of gravitation and mass, or about the nature of the elements, we do not comprehend the *rationale* of the periodic law. It is only by collecting established laws—that is, by working at the acquirement of truth—that we can hope gradually to lift the veil which conceals from us the causes of the mysteries of Nature and to discover their mutual dependency. Like the telescope and the microscope, laws founded on the basis of experiment are the instruments and means of enlarging our mental horizon.

In the remaining part of my communication I shall endeavour to show, and as briefly as possible, in how far the periodic law contributes to enlarge our range of vision. Before the promulgation of this law the chemical elements were mere fragmentary, incidental facts in Nature; there was no special reason to expect the discovery of new elements, and the new ones which were discovered from time to time appeared to be possessed of quite novel properties. The law of periodicity first enabled us to perceive undiscovered elements at a distance which formerly was inaccessible to chemical vision; and long ere they were discovered new elements appeared before our eyes possessed of a number of well-defined properties. We now know three cases of elements whose existence and properties were foreseen by the instrumentality of the periodic law. I need but mention the brilliant discovery of *gallium*, which proved to correspond to ekaaluminium of the periodic law, by Lecoq de Boisbaudran; of *scandium*, corresponding to ekaboron, by Nilson; and of *germanium*, which proved to correspond in all respects to ekasilicon, by Winkler. When, in 1871, I described to the Russian Chemical Society the properties, clearly defined by the periodic law, which such elements ought to possess, I never hoped that I should live to mention their discovery to the Chemical Society of Great Britain as a confirmation of the exactitude and the generality of the periodic law. Now that I have had the happiness of doing so, I unhesitatingly say that although greatly enlarging our vision, even now the periodic law needs further improvements in order that it may become a trustworthy instrument in further discoveries.[6]

I will venture to allude to some other matters which chemistry has discerned by means of its new instrument, and which it could not have made

[6] I foresee some more new elements, but not with the same certitude as before. I shall give one example, and yet I do not see it quite distinctly. In the series which contains Hg = 204, Pb = 206, and Bi = 208, we can guess the existence (at the place VI—11) of an element analogous to tellurium, which we can describe as dvi-tellurium, Dt, having an atomic weight of 212, and the property of forming the oxide DtO_3. If this element really exists, it ought in the free state to be an easily fusible, crystalline, non-volatile metal of a grey colour, having a density of about 9·3, capable of giving a dioxide, DtO_2, equally endowed with feeble acid and basic properties. This dioxide must give on active oxidation an unstable higher oxide, DtO_3, which should resemble in its properties PbO_2 and Bi_2O_5. Dvi-tellurium hydride, if it be found to exist, will be a less stable compound than even H_2Te. The compounds of dvi-tellurium will be easily reduced, and it will form characteristic definite alloys with other metals.

out without a knowledge of the law of periodicity, and I will confine myself to simple substances and to oxides.

Before the periodic law was formulated the atomic weights of the elements were purely empirical numbers, so that the magnitude of the equivalent, and the atomicity, or the value in substitution possessed by an atom, could only be tested by critically examining the methods of determination, but never directly by considering the numerical values themselves; in short, we were compelled to move in the dark, to submit to the facts, instead of being masters of them. I need not recount the methods which permitted the periodic law at last to master the facts relating to atomic weights, and I would merely call to mind that it compelled us to modify the valencies of *indium* and *cerium*, and to assign to their compounds a different molecular composition. Determinations of the specific heats of these two metals fully confirmed the change. The trivalency of *yttrium*, which makes us now represent its oxide as Y_2O_3 instead of as YO, was also foreseen (in 1870) by the periodic law, and it now has become so probable that Cleve, and all other subsequent investigators of the rare metals, have not only adopted it, but have also applied it without any new demonstration to substances so imperfectly known as those of the cerite and gadolinite group, especially since Hildebrand determined the specific heats of lanthanum and didymium and confirmed the expectations suggested by the periodic law. But here, especially in the case of didymium, we meet with a series of difficulties long since foreseen through the periodic law, but only now becoming evident, and chiefly arising from the relative rarity and insufficient knowledge of the elements which usually accompany didymium.

Passing to the results obtained in the case of the rare elements *beryllium*, *scandium*, and *thorium*, it is found that these have many points of contact with the periodic law. Although Avdéeff long since proposed the magnesia formula to represent beryllium oxide, yet there was so much to be said in favour of the alumina formula, on account of the specific heat of the metals and the isomorphism of the two oxides, that it became generally adopted and seemed to be well established. The periodic law, however, as Brauner repeatedly insisted ('Berichte,' 1878, 872; 1881, 53), was against the formula Be_2O_3; it required the magnesia formula BeO—that is, an atomic weight of 9—because there was no place in the system for an element like beryllium having an atomic weight of 13·5. This divergence of opinion lasted for years, and I often heard that the question as to the atomic weight of beryllium threatened to disturb the generality of the periodic law, or, at any rate, to require some important modifications of it. Many forces were operating in the controversy regarding beryllium, evidently because a much more important question was at issue than merely that involved in the discussion of the atomic weight of a relatively rare element; and during the controversy the periodic law became better understood, and the mutual relations of the elements became more apparent than ever before. It is most remarkable that the victory of the periodic law was won by the researches of the very observers who previously had discovered a number of facts in support of the trivalency of beryllium. Applying the higher law of Avogadro, Nilson and Petterson have finally shown that the density of the vapour of the beryllium chloride, $BeCl_2$, obliges us to regard beryllium as bivalent in

conformity with the periodic law.[7] I consider the confirmation of Avdéeff's and Brauner's view as important in the history of the periodic law as the discovery of scandium, which, in Nilson's hands, confirmed the existence of ekaboron.

The circumstance that *thorium* proved to be quadrivalent, and Th = 232, in accordance with the views of Chydenius and the requirements of the periodic law, passed almost unnoticed, and was accepted without opposition, and yet both thorium and uranium are of great importance in the periodic system, as they are its last members, and have the highest atomic weights of all the elements.

The alteration of the atomic weight of *uranium* from U = 120 into U = 240 attracted more attention, the change having been made on account of the periodic law, and for no other reason. Now that Roscoe, Rammelsberg, Zimmermann, and several others have admitted the various claims of the periodic law in the case of uranium, its high atomic weight is received without objection, and it endows that element with a special interest.

While thus demonstrating the necessity of modifying the atomic weights of several insufficiently known elements, the periodic law enabled us also to detect errors in the determination of the atomic weights of several elements whose valencies and true position among other elements were already well known. Three such cases are especially noteworthy: those of tellurium, titanium, and platinum. Berzelius had determined the atomic weight of *tellurium* to be 128, while the periodic law claimed for it an atomic weight below that of iodine, which had been fixed by Stas at 126·5, and which was certainly not higher than 127. Brauner then undertook the investigation, and he has shown that the true atomic weight of tellurium is lower than that of iodine, being near to 125. For *titanium* the extensive researches of Thorpe have confirmed the atomic weight of Ti = 48, indicated by the law, and already foreseen by Rose, but contradicted by the analyses of Pierre and several other chemists. An equally brilliant confirmation of the expectations based on the periodic law has been given in the case of the series osmium, iridium, platinum, and gold. At the time of the promulgation of the periodic law, the determinations of Berzelius, Rose, and many others gave the following figures:—

$$Os = 200;\ Ir = 197;\ Pt = 198;\ Au = 196.$$

[7] Let me mention another proof of the bivalency of beryllium which may have passed unnoticed, as it was published in the Russian chemical literature. Having remarked (in 1884) that the density of such solutions of chlorides of metals, MCl_n, as contain 200 mols. of water (or a large and constant amount of water) regularly increases as the molecular weight of the dissolved salt increases, I proposed to one of our young chemists, M. Burdakoff, that he should investigate beryllium chloride. If its molecule be $BeCl_2$ its weight must be = 80; and in such a case it must be heavier than the molecule of KCl = 74·5, and lighter than that of $MgCl_2 = 93$. On the contrary, if beryllium chloride is a trichloride, $BeCl_3 = 120$, its molecule must be heavier than that of $CaCl_2 = 111$, and lighter than that of $MnCl_2 = 126$. Experiment has shown the correctness of the former formula, the solution $BeCl_2 + 200H_2O$ having (at 15°/4°) a density of 1·0138, this being a higher density than that of the solution $KCl + 200H_2O$ (= 1·0121), and lower than that of $MgCl_2 + 200H_2O$ (= 1·0203). The bivalency of beryllium was thus confirmed in the case both of the dissolved and the vaporised chloride.

The expectations of the periodic law[8] have been confirmed, first, by new determinations of the atomic weight of *platinum* (by Seubert, Dittmar, and M'Arthur), which proved to be near to 196 (taking O = 16, as proposed by Marignac, Brauner, and others); secondly, by Seubert having proved that the atomic weight of *osmium* is really lower than that of platinum, and that it is near to 191; and thirdly, by the investigations of Krüss, and Thorpe and Laurie proving that the atomic weight of *gold* exceeds that of platinum, and approximates to 197. The atomic weights which were thus found to require correction were precisely those which the periodic law had indicated as affected with errors; and it has been proved, therefore, that the periodic law affords a means of testing experimental results. If we succeed in discovering the exact character of the periodic relationships between the increments in atomic weights of allied elements discussed by Ridberg in 1885, and again by Bazaroff in 1887, we may expect that our instrument will give us the means of still more closely controlling the experimental data relating to atomic weights.

Let me next call to mind that, while disclosing the variation of chemical properties,[9] the periodic law has also enabled us to systematically discuss many of the physical properties of elementary bodies, and to show that these properties are also subject to the law of periodicity. At the Moscow Congress of Russian Naturalists in August, 1869, I dwelt upon the relations which existed between density and the atomic weight of the elements. The following year Professor Lothar Meyer, in his well-known paper,[10] studied the same subject in more detail, and thus contributed to spread information about the periodic law. Later on, Carnelley, Laurie, L. Meyer, Roberts-Austen, and several others applied the periodic system to represent the order in the changes of the magnetic properties of the elements, their melting points, the heats of formation of their haloid compounds, and even of such mechanical properties as the coefficient of elasticity, the breaking stress, &c., &c. These deductions, which have received further support in the discovery of new elements endowed not only with chemical but even with physical properties, which were foreseen by the law of periodicity, are well known; so I need not dwell upon the subject, and may pass to the consideration of oxides.[11]

[8] I pointed them out in the *Liebig's Annalen*, Supplement Band., viii. 1871, p. 211.

[9] Thus, in the typical small period of

Li, Be, B, C, N, O, F,

we see at once the progression from the alkali metals to the acid non-metals, such as are the halogens.

[10] *Liebig's Annalen*, Supplement Band., vii. 1870.

[11] A distinct periodicity can also be discovered in the spectra of the elements. Thus the researches of Hartley, Ciamician, and others have disclosed, first, the homology of the spectra of analogous elements: secondly, that the alkali metals have simpler spectra than the metals of the following groups; and thirdly, that there is a certain likeness between the complicated spectra of manganese and iron on the one hand, and the no less complicated spectra of chlorine and bromine on the other hand, and their likeness corresponds to the degree of analogy between those elements which is indicated by the periodic law.

In indicating that the gradual increase of the power of elements of combining with oxygen is accompanied by a corresponding decrease in their power of combining with hydrogen, the periodic law has shown that there is a limit of oxidation, just as there is a well-known limit to the capacity of elements for combining with hydrogen. A single atom of an element combines with at most four atoms of either hydrogen or oxygen: and while CH_4 and SiH_4 represent the highest hydrides, so RuO_4 and OsO_4 are the highest oxides. We are thus led to recognise types of oxides, just as we have had to recognise types of hydrides.[12]

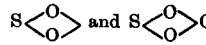
The periodic law has demonstrated that the maximum extent to which different non-metals enter into combination with oxygen is determined by the extent to which they combine with hydrogen, and that the sum of the number of equivalents of both must be equal to 8. Thus chlorine, which combines with 1 atom or 1 equivalent of hydrogen, cannot fix more than 7 equivalents of oxygen, giving Cl_2O_7; while sulphur, which fixes 2 equivalents of hydrogen, cannot combine with more than 6 equivalents or 3 atoms of oxygen. It thus becomes evident that we cannot recognise as a fundamental property of the elements the atomic valencies deduced from their hydrides; and that we must modify, to a certain extent, the theory of atomicity if we desire to raise it to the dignity of a general principle capable of affording an insight into the constitution of all compound molecules. In other words, it is only to carbon, which is quadrivalent with regard both to oxygen and hydrogen, that we can apply the theory of constant valency and of bond, by means of which so many still endeavour to explain the structure of compound molecules. But I should go too far if I ventured to explain in detail the conclusions which can be drawn from the above considerations. Still, I think it necessary to dwell upon one particular fact which must be explained from the point of view of the periodic law in order to clear the way to its extension in that particular direction.

The higher oxides yielding salts the formation of which was foreseen by the periodic system—for instance, in the short series beginning with sodium—

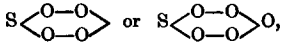
$$Na_2O,\ MgO,\ Al_2O_3,\ SiO_2,\ P_2O_5,\ SO_3,\ Cl_2O_7,$$

must be clearly distinguished from the higher degrees of oxidation which correspond to hydrogen peroxide and bear the true character of peroxides. Peroxides such as Na_2O_2, BaO_2, and the like have long been known. Similar

[12] Formerly it was supposed that, being a bivalent element, oxygen can enter into any grouping of the atoms, and there was no limit foreseen as to the extent to which it could further enter into combination. We could not explain why bivalent sulphur, which forms compounds such as



could not also form oxides such as—



while other elements, as, for instance, chlorine, form compounds such as—

Cl—O—O—O—O—K.

peroxides have also recently become known in the case of chromium, sulphur, titanium, and many other elements, and I have sometimes heard it said that discoveries of this kind weaken the conclusions of the periodic law in so far as it concerns the oxides. I do not think so in the least, and I may remark, in the first place, that all these peroxides are endowed with certain properties obviously common to all of them, which distinguish them from the actual, higher, salt-forming oxides, especially their easy decomposition by means of simple contact agencies; their incapacity of forming salts of the common type; and their capacity of combining with other peroxides (like the faculty which hydrogen peroxide possesses of combining with barium peroxide, discovered by Schoene). Again, we remark that some groups are especially characterised by their capacity of generating peroxides. Such is, for instance, the case in the sixth group, where we find the well-known peroxides of sulphur, chromium, and uranium; so that further investigation of peroxides will probably establish a new periodic function, foreshadowing that molybdenum and tungsten will assume peroxide forms with comparative readiness. To appreciate the constitution of such peroxides, it is enough to notice that the peroxide form of sulphur (so-called persulphuric acid) stands in the same relation to sulphuric acid as hydrogen peroxide stands to water:—

$$H(OH), \text{ or } H_2O, \text{ responds to } (OH)(OH), \text{ or } H_2O_2,$$

and so also—

$$H(HSO_4), \text{ or } H_2SO_4, \text{ responds to } (HSO_4)(HSO_4), \text{ or } H_2S_2O_8.$$

Similar relations are seen everywhere, and they correspond to the principle of substitutions which I long since endeavoured to represent as one of the chemical generalisations called into life by the periodic law. So also sulphuric acid, if considered with reference to hydroxyl, and represented as follows—

$$HO(SO_2OH),$$

has its corresponding compound in dithionic acid—

$$(SO_2OH)(SO_2OH), \text{ or } H_2S_2O_6.$$

Therefore, also, phosphoric acid, $HO(POH_2O_2)$, has, in the same sense, its corresponding compound in the subphosphoric acid of Saltzer:—

$$(POH_2O_2)(POH_2O_2), \text{ or } H_4P_2O_6;$$

and we must suppose that the peroxide compound corresponding to phosphoric acid, if it be discovered, will have the following structure:—

$$(H_2PO_4)_2 \text{ or } H_4P_2O_8 = 2H_2O + 2PO_3.^{13}$$

As far as is known at present, the highest form of peroxides is met with in

[13] In this sense, oxalic acid, $(COOH)_2$, also corresponds to carbonic acid, OH(COOH), in the same way that dithionic acid corresponds to sulphuric acid, and subphosphoric acid to phosphoric; therefore, if a peroxide corresponding to carbonic acid be obtained, it will have the structure of $(HCO_3)_2$, or $H_2C_2O_6 = H_2O + C_2O_5$. So also lead must have a real peroxide, Pb_2O_5.

the peroxide of uranium, UO_4, prepared by Fairley;[14] while OsO_4 is the highest oxide giving salts. The line of argument which is inspired by the periodic law, so far from being weakened by the discovery of peroxides, is thus actually strengthened, and we must hope that a further exploration of the region under consideration will confirm the applicability to chemistry generally of the principles deduced from the periodic law.

Permit me now to conclude my rapid sketch of the oxygen compounds by the observation that the periodic law is especially brought into evidence in the case of the oxides which constitute the immense majority of bodies at our disposal on the surface of the earth.

The oxides are evidently subject to the law, both as regards their chemical and their physical properties, especially if we take into account the cases of polymerism which are so obvious when comparing CO_2 with Si_nO_{2n}. In order to prove this I give the densities s and the specific volumes v of the higher oxides of two short periods. To render comparison easier, the oxides are all represented as of the form R_2O_n. In the column headed Δ the differences are given between the volume of the oxygen compound and that of the parent element, divided by n—that is, by the number of atoms of oxygen in the compound:—[15]

	s.	v.	Δ.		s.	v.	Δ.
Na_2O	2·6	24	−22	K_2O	2·7	35	−55
Mg_2O_2	3·6	22	−3	Ca_2O	3·15	36	−7
Al_2O_3	4·0	26	+1·3	Sc_2O_3	3·86	35	0
Si_2O_4	2·65	45	5·2	Li_2O_4	4·2	38	+5
P_2O_5	2·39	59	6·2	V_2O_5	3·49	52	6·7
S_2O_6	1·96	82	8·7	Cr_2O_6	2·74	73	9·5

I have nothing to add to these figures, except that like relations appear in other periods as well. The above relations were precisely those which made it possible for me to be certain that the relative density of ekasilicon oxide would be about 4·7; germanium oxide, actually obtained by Winkler, proved, in fact, to have the relative density 4·703.

The foregoing account is far from being an exhaustive one of all that has already been discovered by means of the periodic law telescope in the boundless realms of chemical evolution. Still less is it an exhaustive account of all that may yet be seen, but I trust that the little which I have said will account

[14] The compounds of uranium prepared by Fairley seem to me especially instructive in understanding the peroxides. By the action of hydrogen peroxide on uranium oxide, UO_3, a peroxide of uranium, $UO_4,4H_2O$, is obtained (U = 240) if the solution be acid; but if hydrogen peroxide act on uranium oxide in the presence of caustic soda, a crystalline deposit is obtained which has the composition $Na_4UO_8,4H_2O$, and evidently is a combination of sodium peroxide, Na_2O_2, with uranium peroxide, UO_4. It is possible that the former peroxide, $UO_4,4H_2O$, contains the elements of hydrogen peroxide and uranium peroxide, U_2O_7, or even $U(OH)_6,H_2O_2$, like the peroxide of tin recently discovered by Spring, which has the constitution Sn_2O_5,H_2O_2.

[15] Δ thus represents the average increase of volume for each atom of oxygen contained in the higher salt-forming oxide. The acid oxides give, as a rule, a higher value of Δ, while in the case of the strongly alkaline oxides its value is usually negative.

for the philosophical interest attached in chemistry to this law. Although but a recent scientific generalisation, it has already stood the test of laboratory verification, and appears as an instrument of thought which has not yet been compelled to undergo modification; but it needs not only new applications, but also improvements, further development, and plenty of fresh energy. All this will surely come, seeing that such an assembly of men of science as the Chemical Society of Great Britain has expressed the desire to have the history of the periodic law described in a lecture dedicated to the glorious name of Faraday.

APPENDIX III.

NOTE ON THE DISCOVERY OF HYDRO-NITROUS ACID, N_3H. (HYDROGEN NITRIDE, AZOIMIDE).

BY PROFESSOR MENDELÉEFF.

EXTRACTED FROM THE JOURNAL OF THE RUSSIAN PHYSICO-CHEMICAL SOCIETY, VOL. XXII. 1890, NO. 8.

AMONG the brilliant discoveries made in chemical science during the current year, we must number, besides the preparation of the compound $Ni(CO)_4$,[1] the discovery made by Curtius ('Ber' 23, 3023), who demonstrated the existence of the compound N_3H, the mode of its preparation, and its analogy with the halogen acids. Although I have not published any paper respecting the possibility of the existence of such a compound, still I have foreseen it in consequence of the considerations developed in my communication on the nitriles to the first meeting of the Russian naturalists (1867), and in the first edition (1868–1870) of my 'Principles of Chemistry.' I think it may not be superfluous to publish these considerations now, because in my opinion they may help to explain the structure of the compound N_3H, and to indicate the position which it should occupy among the other known compounds of nitrogen,[2] and

[1] The composition and properties of $Ni(CO)_4$ investigated by Langer, Mond, and Quincke are so new, instructive, and important for the periodic system of the elements that, owing to the possibility of obtaining such unexpected substances, a fresh stimulus has arisen for the reinvestigation of the data respecting the properties of the most common elements. And I think many important discoveries, like that made by Curtius, may still be looked for in the provinces of sulphur and nitrogen.

[2] As nitrogen gives gaseous molecules NO, NH_5, and NO_2, which contain one atom of nitrogen, therefore the nitrogen in them is either bi- or tri- or quadrivalent compared with hydrogen. And, as this element forms also molecules N_2O, N_2O_4, and N_2O_5, which contain two atoms of nitrogen, therefore N_2 appears to be equal to H_2, H_3, and H_{10}. In NH_4Cl, $NO_2(OH)$, and other compounds, the nitrogen is seen to be quinquivalent. These considerations alone, without entering into details, show that the compounds of nitrogen cannot be understood by the acceptance of that method of building up molecules from atoms having a constant valency which the 'structuralists' consider sufficient for the comprehension of the formation of nearly all carbon compounds (CO forms an universally known exception). For this reason I think that the study of the compounds of nitrogen,

perhaps also help to point out the reactions and new methods of preparation of this remarkable acid, whose existence should tend to throw a light on the nature of the metallic compounds of nitrogen, many points as to which are not clear. But in order to render clear the conclusions arrived at, it will be necessary to touch on certain general conceptions connected with the periodic system.

If an element R gives a compound RX_n with univalent elements X—for example, with the halogens—then the corresponding salt-forming hydrate will be $RO_{\frac{n}{2}}^{m}(OH)_{n-m}$, in which, however, the total number of oxygen atoms never exceeds four, because it is one of the peculiarities of the periodic system that it shows a correspondence (1) between the composition of the hydride and that of higher salt-forming oxides of all elements, and (2) between the composition of the hydrates and hydrogen compounds. If an element R forms RH, then it gives oxides of the composition R_2O to R_2O_7, and hydrates from ROH to RHO_4 or $RO_3(OH)$, as the salt-forming oxides and hydrates; to an element which forms RH_2 there correspond the higher oxides RO_3 and RH_2O_4 or $RO_2(OH)_2$; and to those elements which give RH_3 there correspond the higher salt-forming hydrate RH_3O_4 or $RO(OH)_3$, and consequently the higher oxide R_2O_5, &c. These now universally known relations may be expressed thus: (1) the sum of the valencies of hydrogen and oxygen atoms (in the higher salt-forming oxide) which can combine with any element is equal to eight (for instance, SH_2 and SO_3; PH_3 and P_2O_5); (2) the number of atoms of oxygen in the higher salt-forming hydrate is four—for example, $HClO_4$, H_2SO_4, H_3PO_4—and, as a consequence of the first two conclusions, (3) the maximum amount of hydrogen in the salt-forming hydrates of the oxides does not exceed the amount of hydrogen in the hydride of the element when the hydride is a gaseous compound of the formula RH_n.

Hence it is evident, firstly, that an element R, which, like nitrogen for example, forms compounds RH_3 and R_2O_5, or in general RX_3 and RX_5, does not form a saline hydrate $R(OH)_5$, although $R(OH)_3$ is capable of existence. Secondly, that even the highest hydrate RH_3O_4 may lose a portion of this water, and give incomplete hydrates, such as $PH_3O_4 = PO(OH)_3$: $P_2H_4O_7 = [PO(HO)_2]_2O$ and $PO_2(OH)$, for example. Thirdly, that the normal

and especially of those which pass into vapour and resemble the compound N_3H, should not only lead to the extension of our experimental data, but also aid the progress of that theory of chemical structure which started almost exclusively from data respecting the carbon compounds, in which the type CX_4 appears with particular force owing to the fact of its giving CH_4 and CO_2 as limiting compounds of equal valency. In nitrogen, which gives NH_3 and N_2O_5 (likewise in sulphur, which forms SH_2 and SO_3), there is no longer this equality, and in the sense of the periodic law there cannot be, and therefore the further perfection of the conception of the chemical structure of molecules can be looked for sooner in the compounds of this element than in those of carbon. In this paper I endeavour to avoid the formulation of the conception touching on this aspect of hydronitrous acid, and I will here only compare N_3H and H_3N in order to show the equivalence of N_2 and H_2 as well as of the atoms in a free state, for both gases give molecules N_2 and H_2. Therefore, guided by those conceptions of substitutions which have been given by me in my London lecture (Appendix I.) we may expect to obtain N_2H_2, as a combination of the residues of N_3H and NH_3. If N_2H_2 be obtained, then the series: NH_3, N_2H_2, and N_3H will give a much greater insight into the internal properties of nitrogen than the common recognition of this element as quadri-, tri-, or quinqui-valent.

ammonium salts of any element must correspond with the hydrates of that element, and consequently may contain oxygen atoms other than those which unite the ammonium radicles to the element R; as, for example, in $NO_2(ONH_4)$, $SO_2(OH)(ONH_4)$, $CO(OH)(ONH_4)$, $CO(ONH_4)_2$, $COH(ONH_4)$, &c.

Such ammonium compounds, on losing water, yield amides and nitriles. If the loss of water is limited by the passage of the residue ONH_4 into NH_2, then amides are produced; for example, formamide, $CO(NH_2)H$, corresponds with ammonium formate, $CO(ONH_4)H$.

If the oxygen and hydrogen are evolved from the amides in the form of water, which can only take place in the above-mentioned ammonium salts which contain an excess of oxygen (for example, $NO_2 \cdot ONH_4$, &c.), then *nitriles* are formed. Thus to nitric acid there corresponds the nitrile NON, or nitrous oxide, N_2O, and to formic acid there corresponds the nitrile CNH, or hydrocyanic acid, and in general the amides, $RCO \cdot NH_2$, and nitriles, $R \cdot CN$, or cyanides, correspond with the carboxyl compounds, $R \cdot COOH$. The amide corresponding with acid ammonium sulphate, $SO_2(OH)(ONH_4)$, will contain $SO_2(OH)(NH_2)$; and the nitrile SO_2HN, of which there may, moreover, be two possible isomerides; $SO_2{:}NH$, in which the hydrogen is governed or held by the nitrogen—*i.e.* where it exists as the ammonia residue NH (imidogen), which is united by two bonds with the SO_2 group; the other, SO(OH)N, in which the hydrogen is held as hydroxyl.[3]

As the nitriles are formed by a dual loss of molecules of water, they are able, firstly, to combine twice with various other molecules; secondly, to combine among themselves; and thirdly, to polymerise into di- and tri-polymerides; for example, to the nitrile of carbonic acid (cyanic acid), CHON, corresponds the polymeric form $C_3H_3O_3N_3$, cyanuric acid.

It is evident that if we regard as perfect hydrates only such as contain a given element in union with hydroxyl only—for example, $Na(OH)$, $Ti(OH)_4$, &c.—then nitriles can only be expected to be obtained from imperfect hydrates, such as $SO_2(OH)_2$, $PO(OH)_3$, &c.

As amides are equal to hydrates $+ NH_3 - H_2O$, it is obvious that there must be an analogy and equivalency between the direct combination of water and ammonia. And therefore direct combinations with ammonia essentially proceed under the influence of the same forces as produce hydrates, and the compounds produced should show the properties of amides. If sulphuric anhydride combine with ammonia, forming amido-compounds, then a similar character should be ascribed to the compounds of salts with ammonia, which is not only confirmed in the cobalt-ammonium and similar compounds, but even in the direct absorption of ammonia by many salts—for example, by calcium chloride, copper sulphate, &c. And as $CuSO_4$ absorbs $5NH_3$, just as it also combines with $5H_2O$, we see in the quantitative aspect of this, as in many other examples, a confirmation of the above-mentioned correlation between the compounds of ammonia and water.

[3] Although I am obliged, for the want of other means of expression, to speak of the bonds of elements, still I do not understand them in the general statical sense of this word, but in that dynamical sense which I endeavoured to express in my above-mentioned London lecture (Appendix I.).

It is necessary to take all these facts[4] into consideration, in order that the representation respecting hydronitrous acid, N_3H, should be understood. We must first of all turn to the ammonium compounds of nitric acid as a starting point. And in order that all the relations should be more self-evident, we will start from the anhydrides of nitric and phosphoric acids.

As nitrogen and phosphorus give NH_3 and PH_3, their highest possible hydrates are—

Meta-	N_2O_5,H_2O and $P_2O_5,H_2O = 2PO(OH)_3 - 2H_2O$
Pyro-	$N_2O_5,2H_2O$ and $P_2O_5,2H_2O = 2PO(OH)_3 - H_2O$
and Ortho-	$N_2O_5,3H_2O$ and $P_2O_5,3H_2O = 2PO(OH)_3$.

The perfect hydrates, on the other hand—for example, $N_2O_5,5H_2O = 2N(OH)_5$—belong to those unstable compounds which are generally simply regarded as solutions.[5] The ortho- and pyro-hydrates of nitric acid must also be regarded as unstable compounds, whereas the corresponding derivatives of phosphorus have long been known as distinct and individual hydrates, on account of the existence of the corresponding salts. As, on the other hand, in its basic mercury and lead salts[6] nitric acid shows a tendency to form ortho-salts, the fact that nitrogen compounds analogous to hydrogen disodium phosphate, $PO(OH)(ONa)(ONa)$, cannot be easily produced is simply one of the peculiarities which distinguish nitrogen from phosphorus, and which show the relative stability of phosphoric anhydride and ammonia as compared with nitric anhydride and phosphine, PH_3. It may, therefore, be considered probable that in addition to the ordinary or ammonium meta-nitrate, $NO_2{\cdot}ONH_4$, the ammonium pyro- and ortho-nitrates, or di- and tri-ammonium compounds, $NO(OH)(ONH_4)_2$ and $NO(ONH_4)_3$, and their corresponding amides or anhydro- derivatives $NO_2(ONH_4),NH_3$, and $NO_2(ONH_4),2NH_3$, are capable of existence. Thus the latter is the ortho- salt, $NO(ONH_4)_3$, deprived of water. Both these anhydro-ammonium compounds have in fact been described by Divers (1872), who considered them to be solutions in which the tendency of ammonium nitrate to liquefy anhydrous ammonia[7] is exhibited; but in the following year Raoult proved that the liquid produced in this way has a definite composition $NO_2(NH_4O),2NH_3$, and that between $-10°$ and $+28°$ it is decomposed into a definite solid compound $NO_2(ONH_4),NH_3$, which in turn is readily dissociated when heated, with liberation of ammonia.[8]

[4] They are more fully developed in the body of this work.

[5] In my work on *The Investigation of Aqueous Solutions According to their Specific Gravity*, 1887, p. 361, it is shown that at present, so long as there are no more accurate determinations for the specific gravities of nitric acid, we must, on the basis of the variation of the density of the solutions, recognise the existence of a hydrate $HNO_5,2H_2O$ which is nothing else than $N(OH)_5$ or $N_2O_5,5H_2O$.

[6] This vol. pp. 51 and 133.

[7] This is one of the many historically instructive examples which prove that at present only an artificial distinction is made between solutions and definite compounds, and that there is no real fundamental difference.

[8] The explanation of the combination of ammonia with ammonium nitrate may be applied to a number of other cases of the combination of ammonia with salts, and may even explain the different degrees of stability of such compounds. These considerations

These compounds, then, the existence of which was rendered probable from the conclusions arrived at above, correspond with the imperfect hydrates (ortho-, meta-, and pyro-) of nitric acid, and must therefore have, in certain respects, the character of amides,[9] in which case it is to be expected that they would be converted into nitriles by the further loss of the elements of water. Assuming the elimination of water to be as complete as possible, we should obtain—

From $NH_4NO_3 - 2H_2O$ the nitrile N_2O.
„ $NH_4NO_3NH_3 - 3H_2O$ the nitrile N_3H.
„ $NH_4NO_32NH_3 - 3H_2O$ the nitrile N_4H_4.

The first of these substances has long been known as nitrous oxide, and the two others have now been obtained by Curtius in the form of hydronitrous acid and its ammonium salt, N_3NH_4.

Having thus enunciated the relations that I consider to exist between the substances discovered by Curtius and the views deduced by me from the periodic law, and having shown the relations in which the newly-discovered substances stand to the other nitrogen compounds, I consider it necessary to turn to the properties of hydronitrous acid, which at first sight seem very unexpected, but which may, however, be sufficiently explained on the basis of the above representations.[10]

We must first turn our attention to the quantitative aspect of the subject —that is, to the fact that amides and nitriles proceed from ammonium salts, in which the presence of ammonium, with its four atoms of hydrogen, must be recognised. Therefore it may be supposed that two of these atoms of hydrogen are eliminated in the form of water in the formation of amides, and the remaining two in the further loss of water—that is, in the passage of the amides into nitriles. And therefore—

The simplest and most plausible representation of the conversion of ammonium salts into amides and nitriles consecutively is obtained by the supposition that, in the first place, the elements of water are eliminated solely at the expense of the hydrogen of the ONH_4 group; it is in this way

oblige one to seek for amide reactions in those numerous compounds which are known between salts and ammonia.

[9] This may be expressed by formulæ; for example, for the ortho-compounds (with $2NH_3$) by separating the groups (NH_2), thus $NO_2(ONH_4),2NH_3 = NO(ONH_4)(ONH_4)(NH_2)$. The mono-ammonium compound, if its formula be not doubled (to make it correspond with the pyro-salt), will be $NO_2(ONH_4)NH_3 = NO(ONH_4)(OH)(NH_2)$, and if this be true, one would expect salts $NO(ONH_4)(OM)(NH_2) = MNO_3,2NH_3$, and the formation of ethylene, acetylene, and other corresponding derivatives.

[10] In one of my unpublished notes, dated 1871 or 1872, after having expressed the composition of N_3H and N_4H_4, I directly presupposed that, if these bodies were able to exist and did not polymerise, they would be an acid, and a salt which (like $CNONH_4$) would suffer intramolecular change and pass into a symmetrical amide, $NH_2{\cdot}N{:}N{\cdot}NH_2$ (like urea). The improbability of their composition, and the small probability of these substances existing in a stable form, together with the fact that I was then occupied with other subjects, kept me from publishing my hypothetical reflections, the essence of which I now communicate, although I know that, *post factum*, they have not the same significance which they would have had, had they been published in 1871 or 1872.

that all acid amides are produced. For example, if an organic acid have the composition RCOOH, then its ammonium salt is $RCOONH_4$, and its amide should be expressed by $RCONH_2$. When, however, the oxygen of the ONH_4 and OH groups has been taken away, any further loss of water can only take place by the combination of the hydrogen in the amido-group with the oxygen contained in the acid radicle. Thus in the above example of an organic acid, the transformation of the amide into the nitrile can only be accomplished by the formation of water at the expense of the NH_2 and CO groups, and therefore the nitriles of such acids have the structure of cyanogen compounds, $RC^{\equiv}N$; this, as is well known, is verified by experiment.

On applying these considerations to the formation of hydronitrous acid, we find that it is necessary to start from ortho-nitric acid, NO(OH)(OH)(OH), or rather from the corresponding di-ammonium salt, $NO(OH)(ONH_4)(ONH_4)$, which, judging from the above, by the elimination of four molecules of water, gives water at the expense of all the contained oxygen, and of the hydrogen of the ammonium—that is, there is formed NHNN, in which two of nitrogen remain from ammonium groups, and only one atom of nitrogen from nitric acid, whilst the hydrogen atom also belongs to the elements of ortho-nitric acid.[11] Hence this hydrogen should have the same character as in acids, and not as in ammonia; considering also the energetic acid property of nitric and nitrous acids—compared with carbonic acid, for example, and the position occupied by nitrogen in the periodic system which assigns to it more marked acid-forming properties than carbon—it follows that the compound N_3H should have a distinctly acid character, being a nitrile. This conclusion is based on the fact that hydrocyanic acid, the nitrile of formic acid, has a distinctly acid character, notwithstanding that the hydrogen atom of the nitrile, when forming a component of the molecule of formic acid, is not replaceable by metals, and that it is under the influence of carbon—a feebler acid-forming element than nitrogen. The hydrogen atom in hydrocyanic acid has evidently acquired a feeble acid character under the influence of the nitrogen and carbon as acid elements.[12] And since the hydrogen atom in hydronitrous acid is in combination only with such a distinctly acid element as nitrogen, it should acquire the property of being replaceable by metals, even to a greater degree than the hydrogen atom in hydrocyanic acid, so

[11] According to the hypothesis of the structuralists the structure of hydronitrous acid may, in this sense, be expressed by taking one of the component nitrogen atoms as quinquivalent, and united to H and 2N by its five affinities, and both the other atoms of nitrogen as trivalent, and united together by one affinity. It may be more simply, but just as hypothetically, supposed that one nitrogen is trivalent and uniting both H and 2N by its affinities, and supposing that these two nitrogens are univalent, as in nitrous oxide, N_2O. The latter mode of representation expresses the near relation existing between nitrous oxide and hydronitrous acid, as: $NH_3 + N_2O = H_2O + NHN_2$.

[12] The fact that carbon has a distinct, although feeble, acid character is easily seen in the hydrocarbons containing a small amount of hydrogen (for instance, acetylene), because the hydrogen of such hydrocarbons is replaceable by metals. The connection between acetylene and hydrocyanic acid is beyond doubt. Besides which, it is known from L. N. Shiskoff's researches that nitroform, or trinitromethane, $CH(NO_2)_3$, has sharply defined acid properties, owing evidently to the presence of such acid elements as the nitro- group and carbon.

that the compound N_3H must have the properties of an acid. That nitrogen has a more distinctly acid character than carbon is also seen from the fact that the hydrogen in ammonia is more readily and directly replaced by metals—for instance, by sodium—than the hydrogen in marsh gas or ethane; this is mainly due to the different nature of nitrogen and carbon, as is also expressed by their respective positions in the periodic system of the elements.

Thus it seems to me that the acid character of N_3H is as easily understood as that of hydrocyanic acid, although they are both nitriles.

If hydronitrous acid is really a nitrile it should, like the cyanogen compounds, have many peculiar properties. As certain of these relations have not yet been investigated for hydronitrous acid, I think it will not be superfluous, in passing, to mention those which, in my opinion, may be found to a greater or less extent in a further research into the substances discovered by Curtius.

The most remarkable properties shown by the cyanides are: (1) Polymerisation; for example, the formation of cyanuric acid, solid cyanogen chloride, &c. (2) The faculty of giving complex compounds (for example, the formation of stable double salts like $K_4FeC_6N_6$); and (3) Isomerism—for instance, the passage of ammonium cyanate into urea, &c.—which for a long time confused the study of these compounds, but which can now be foreseen from the fact that the cyanides are substances which can proceed from the loss of water from ammonium salts. Thus the faculty of forming polymerides and complex salts should be understood as a propensity to combine with foreign molecules in the place of those molecules of water which have been separated in the formation of cyanides.

Properties resembling these, with certain individual differences, should be met with in the nitriles of nitric acid, or in the compounds discovered by Curtius, if they are nitriles, as may be thought from the above.

For example, the ammonium salt of hydronitrous acid, $N_3{\cdot}NH_4$, as a clearly asymmetrical compound, to a certain extent analogous to ammonium cyanate, will probably under certain circumstances (perhaps on heating its solution) undergo intramolecular change and be converted into a symmetrical amide $NH_2{\cdot}N{:}N{\cdot}NH_2$, corresponding with the amido-nitrile of tri-ammonium orthonitrate, $NO(ONH_4)(ONH_4)(ONH_4)$.

Equally to be desired would be a research on the double salts of hydronitrous acid, all the more as the general character (*e.g.* the insolubility of the silver salt) of the salts of this acid recall the properties of the cyanides. If we suppose, for instance, that it forms a double salt with iron and potassium, then it will probably give a series of characteristically-coloured salts like the ferrocyanides, and also a series of compounds corresponding with prussian blue, Fe_nN_{3n}, which, if capable of existence in a hydrate, would doubtless be explosive.

As regards the faculty of hydronitrous acid and its derivatives for polymerisation, it may be assumed that this is already indicated by the behaviour of the analogous compounds of phosphorus. This is probably connected with the fact that phosphorus, the analogue of nitrogen, polymerises more easily than it, as is seen not only in the varieties of ordinary and red phos-

phorus, but also in the fact that the molecule of phosphorus vapour, even at very high temperatures, contains P_4, and does not give P_2, whilst nitrogen is only known in the state of N_2. In fact, as the vapour density of chlorphosphamide (Gladstone, Wichelhaus) indicates a molecule of the form $P_3N_3Cl_6$, so also phospham is probably a polymeride of the composition $(PN_2H)_n$, and not an exact analogue of hydronitrous acid, although it offers some resemblance to it, inasmuch as it contains the elements in the ratio PHN_2.[13]

At all events, the further investigation of hydronitrous acid and its derivatives should be the means of throwing much light on our store of knowledge of the nature of nitrogen and its compounds—that is, it is desirable that this subject should be worked out in all its details, and there is reason to think that this would much aid the further progress of all chemical data.

[13] An examination of the composition and properties of phospham given by me in the *Principles of Chemistry* (1st edition), was the natural source from which I arrived at the prediction of the existence of NHN_2 which I mentioned above.

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TABLE IV.

The Atomic Weights of the Elements

Distribution of the Elements in Periods

Groups	Higher Salt-forming Oxides	Typical or 1st small Period	Large Periods				
			1st	2nd	3rd	4th	5th
I.	R_2O	Li = 7	K 39	Rb 85	Cs 133	—	—
II.	RO	Be = 9	Ca 40	S 87	Ba 137	—	—
III.	R_2O_3	B = 11	Sc 44	Y 89	La 138	Yb 173	—
IV.	RO_2	C = 12	Ti 48	Zr 90	Ce 140	—	Th 232
V.	R_2O_5	N = 14	V 51	Nb 94	—	Ta 182	—
VI.	RO_3	O = 16	Cr 52	Mo 96	—	W 184	Ur 240
VII.	R_2O_7	F = 19	Mn 55	—	—	—	—
VIII.			Fe 56	Ru 103	—	Os 191	—
			Co 58·5	Rh 104	—	Ir 193	—
			Ni 59	Pd 106	—	Pt 196	—
I.	R_2O	H = 1. Na = 23	Cu 63	Ag 108	—	Au 198	—
II.	RO	Mg = 24	Zn 65	Cd 112	—	Hg 200	—
III.	R_2O_3	Al = 27	Ga 70	In 113	—	Tl 204	—
IV.	RO_2	Si = 28	Ge 72	Sn 118	—	Pb 206	—
V.	R_2O_5	P = 31	As 75	Sb 120	—	Bi 208	—
VI.	RO_3	S = 32	Se 79	Te 125	—	—	—
VII.	R_2O_7	Cl = 35·5	Br 80	I 127	—	—	—
		2nd small Period	1st	2nd	3rd	4th	5th
			Large Periods				

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